

IV.C.4 The Quantum Effects of Pore Structure on Hydrogen Adsorption

Raina Olsen
 Oak Ridge National Laboratory
 One Bethel Valley Road
 P.O. Box 2008, MS-6115
 Oak Ridge, TN 37831-6115
 Phone: (573) 999-2371
 Email: olsenrj@ornl.gov

DOE Managers
 Channing Ahn
 Phone: (202) 586-9490
 Email: Channing.Ahn@ee.doe.gov
 Ned Stetson
 Phone: (202) 586-9995
 Email: Ned.Stetson@ee.doe.gov

Technical Advisor
 James Morris
 Phone: (865) 630-0020
 Email: morrisj@ornl.gov

Project Start Date: October 31, 2011
 Project End Date: October 30, 2013

Technical Barriers

This project addresses the following technical barrier from the Hydrogen Storage section (3.3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

Technical Targets

This project studies a class of Saran carbon adsorbents with unusually high volumetric storage (Table 1) compared to similar carbons. The samples were synthesized and measured by the Alliance for Collaborative Research in Alternative Fuel Technology (ALL-CRAFT) group at the University of Missouri [1-3] during preliminary work.

FY 2013 Accomplishments

- Characterization of the samples of interest with X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), and CO₂ adsorption, which shows evidence for narrow graphitic pores [4]
- Discovery of a temperature dependent phase transition to an exceptionally high density phase in the samples of interest, based on evidence from hydrogen isotherms and small angle neutron scattering (SANS) spectra
- Proposed theoretical model of a significant, highly novel quantum effect for H₂ adsorbed in a model pore consistent with the experimental properties of the samples of interest [5]
- Analysis of experimental inelastic neutron scattering data [6,7] and calculation of the quantum states of H₂ adsorbed in graphene slit-pores, resulting in better understanding of the quantum behavior of adsorbed H₂



Overall Objectives

- Understand how quantum effects may be used to increase hydrogen storage
- Measure properties of a sample with unusually high volumetric hydrogen storage

Fiscal Year (FY) 2013 Objectives

- Materials characterization
- Analysis of inelastic neutron scattering data
- Theoretical solution of quantum states of hydrogen adsorbed in expanded graphite pores

TABLE 1. Volumetric and gravimetric performance of a representative Saran carbon (HS;0B) compared with an industry standard activated carbon (MSC-30).

Characteristic	Units	2017 Target (System)	2017 Target (Material)	HS;0B		MSC-30	
				300 K 90 bar	80 K 90 bar	300 K 90 bar	80 K 90 bar
Volumetric Storage	g H ₂ /L sample	40	~80	14.7	58.4	8.50	41.6
Gravimetric Storage	wt% (g H ₂ /g system *100)	5.5	~11	1.22	4.68	2.21	9.90

INTRODUCTION

No current hydrogen storage method is able to simultaneously meet the 2017 gravimetric and volumetric system targets. There are two competing types of material solutions. Chemical systems hold the H_2 in a much smaller volume with strong bonds, but their weight is generally too large. Adsorbents hold the H_2 on a lighter high surface area material with weaker forces which are not able to squeeze the molecules much closer together than they are in liquid H_2 , but this density is not high enough to meet volumetric targets. It seems unlikely that either the 2017 or ultimate targets will be met without a radically different approach to the problem.

The ALL-CRAFT group at the University of Missouri has produced a class of Saran nano-porous carbon adsorbents with several unusual and desirable characteristics [1-4]. In particular, their volumetric storage is 40-75% higher than the best alternative carbons (Table 1). While the gravimetric performance is 45-55% smaller than other carbons, it is notable that these values are achieved with sample surface areas of $\sim 700 \text{ m}^2/\text{g}$, nearly a quarter of typical high-performing carbons. The high adsorption per unit surface area originates from the apparent ability of the material to store the adsorbed H_2 at approximately twice the density of liquid H_2 , which is theoretically impossible according to classical adsorption models. If a higher surface area material with the same performance samples could be synthesized, it could simultaneously meet gravimetric and volumetric system targets at cryogenic temperature, while possessing all of the other advantageous properties of a carbon adsorbent which are helpful in meeting and exceeding targets for system cost, durability, safety, refueling time, and thermal management.

APPROACH

Two assumptions provide the foundation of this project. The first is that preliminary data on the samples of interest [1-3] is reasonably correct and there are indeed novel physical mechanism(s) at work in these materials which can be utilized to increase hydrogen storage performance. The second is that there is a link between the unique properties of the samples which were observed during preliminary work. These include the high magnitude of cryogenic H_2 adsorption as well as the shape of the isotherms, the structural properties of the samples such as their narrow distribution of small pores, and the measured differences between quantum states for H_2 adsorbed in one of the samples of interest compared to H_2 adsorbed in three other carbon materials [2,7].

Rather than making new materials, hoping for slight improvements, the focus of this project has been on understanding these samples so that significantly better materials can be intelligently designed. The initial assumptions led to a hypothesis that there are some significant quantum effect(s) which are highly dependent on

pore structure and able to significantly increase hydrogen adsorption. A combination of theory and experiment has been used to explore this hypothesis, seeking insight into the sample structure, verifying that there are indeed unique and desirable mechanism(s) at work, probing their properties, and exploring their theoretical basis.

RESULTS

Characterization of the sample of interest [4] shows it is highly graphitic. XRD spectra, shown in Figure 1(a), show a large graphite 002 peak, though its broadness indicates significant disorder. Pore size distributions were calculated from CO_2 isotherms (Figure 1(b)) and show mainly pores $< 1 \text{ nm}$. TEM images show a significant amount of disordered graphite, and pores which form where graphene layers split apart [4]. But the pore shown in Figure 1(c) was the smallest observed; most were $> 1 \text{ nm}$ in width. One may hypothesize that the unseen $< 1 \text{ nm}$ pores lie parallel to the planar dimension of the flaky sample grains [2,4] and thus parallel to the TEM field of view. If these pores are similarly formed where graphene layers split apart, they might likely be constrained by the thinness of the flake to be narrower and flatter than observed pores. Thus the sample is graphitic with narrow pores, and graphene slit-pores are a plausible model.

It is important to validate the H_2 isotherms (Figure 2) originally measured by ALL-CRAFT at 80 and 90 K [1-3]. The unusual behavior has been observed in three Saran samples synthesized with similar procedures measured by ALL-CRAFT. However, these unusual properties (lack of a peak in the cryogenic gravimetric excess and high overall amounts) can easily be the result of “null” calibration errors in volumetric measurements [8]. A sample of HS;0B-20 was sent to the National Renewable Energy Laboratory (NREL) for measurement of a H_2 isotherm at $\sim 76 \text{ K}$ in a liquid N_2 bath. The NREL isotherm (Figure 2, bottom) is typical in magnitude and shape for a low surface area carbon with narrow pores. ALL-CRAFT also measured this sample in a liquid N_2 bath, finding very good agreement with the NREL data. There are two possible explanations for these results. The first is that the original measurements were wrong and the new measurements are correct. The second is that all isotherms are reasonably correct, and there is a temperature dependent phase change between a classical adsorbed phase and a novel high density phase. This hypothesis is supported by the original measurements of HS;2B, which showed a typical isotherm at 80 K and the unusually high adsorption at 90 K. Additionally, HS;0B and HS;2B were measured sequentially with the same calibration, but no single value for the calibration error [8] at 80 K results in good agreement between the corrected isotherms of these otherwise similar samples. The instrument was also validated near the time of these measurements by comparison of NREL and ALL-CRAFT isotherms for two activated carbons [1].

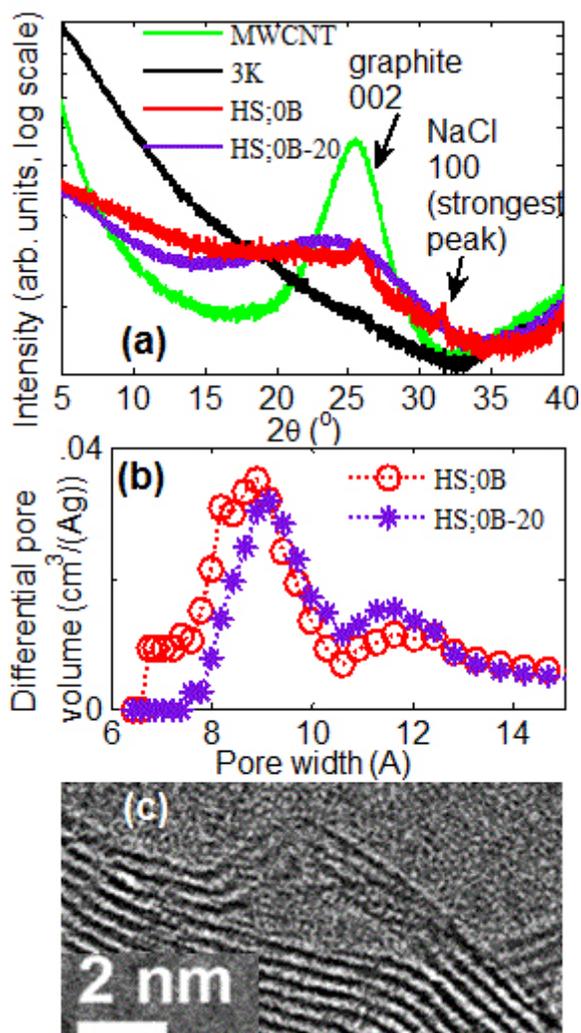


FIGURE 1. Materials characterization of Saran carbon HS:0B and variants, activated carbon 3K, and multi-walled carbon nanotubes (MWCNTs). (a) XRD spectra (b) Pore size distributions calculated from CO₂ adsorption isotherms. (c) Bright field TEM image of HS:0B.

SANS was used to look for evidence of the proposed phase transition. SANS is sensitive to surfaces or interfaces between different materials and has previously been used to study the amount of H₂ in carbon adsorbents [9]. Because the coherent scattering length is positive for C and negative for H, the surface contrast and thus the SANS intensity increases monotonically as hydrogen is adsorbed in carbon pores. Collected spectra also contain an incoherent component linearly proportional to the amount of hydrogen in the sample cell. Spectra are shown in Figure 3(b) for H₂ adsorbed in HS:0B and 3K, an activated carbon with typical properties. Hydrogen pressure was held fixed at ~104 bar while the temperature was varied between ~55-115 K. For a classical system, the amount of hydrogen in the cell (including the adsorbed and gas phases) and thus the scattering intensity should drop monotonically as the temperature rises. For

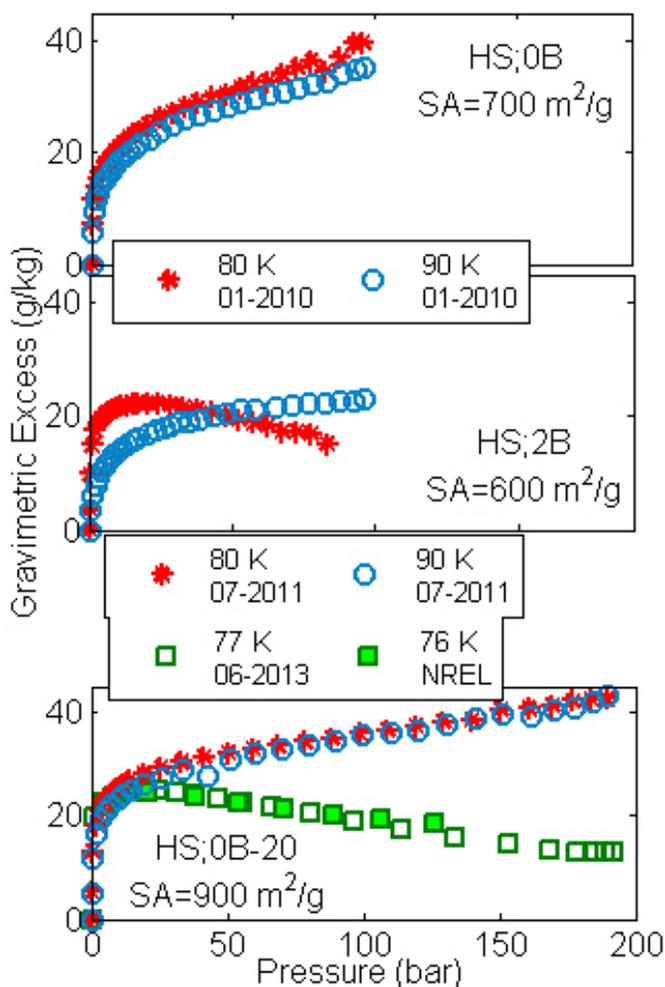


FIGURE 2. Gravimetric excess hydrogen adsorption, in grams H₂ per kilogram of sample, for three variants of a Saran carbon. Except where noted, all isotherms were collected by the ALL-CRAFT group using a Hiden HTP1 volumetric analyzer, with the month and year of the measurement noted in the captions. The NREL measurement was done in 06-2013.

sample 3K, the expected result is obtained. But for HS:0B, the SANS intensity increases between 80 K and 90 K, the same approximate temperature range over which the measured H₂ isotherms show evidence of a transition to a high density phase (Figure 2).

Theoretical work has explored the many-body quantum problem of H₂ in narrow graphene slit-pores [5]. In these pores, there is a special “staggered” quantum state in which the H₂ hops back and forth between the top and bottom of the pore as it travels along the surface (Figure 4(a)). This state has a pair-correlation function (Figure 4(b)) similar to liquid H₂ [10]. Thus, this quantum state mimics the natural form taken by H₂ at high density to minimize its inter-molecular interactions, but in a single delocalized quantum state that extends over the entire pore rather than in many individual

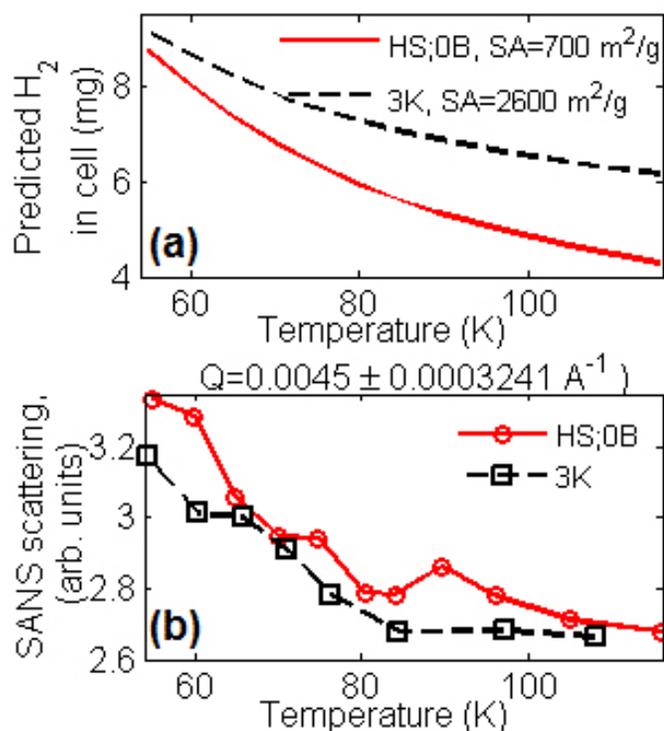


FIGURE 3. SANS measurements of H₂ adsorbed in two porous materials: Saran carbon HS:0B and activated carbon 3K. Temperature was varied as pressure was held constant at 105.1 ± 0.4 bar for HS:0B and 102.7 ± 0.1 bar for 3K. (a) Estimated amount of H₂ in the sample cell, calculated by assuming that because of the high pressure and low temperature, the adsorption surfaces hold a full monolayer of H₂ at all temperatures studied while the gas density drops as the temperature rises. (b) SANS intensity at a neutron momentum transfer $Q=0.0045 \text{ \AA}^{-1}$ for H₂ adsorbed in each sample. Error bars are the size of the symbols. A small value of Q , corresponding to a large wavelength, was used to reduce the effect of Å-scale variations in the H₂ density inside the pores.

quantum states localized at different positions. Due to the hopping motion, the staggered state has non-zero kinetic energy (Figure 4(c)). But as coverage increases, the ability of this state to minimize the interaction energy makes it much lower in energy than any other state (Figure 4(d)). Preliminary calculations show this energy difference is large enough to form a Bose-Einstein condensate (BEC) at temperatures up to 60 K in narrow pores with widths from 7.3-8.9 Å. A BEC is a unique quantum form of matter in which many particles occupy the same quantum state, and has never been observed above 2.2 K. Thus this work [5] predicts a highly novel quantum effect in pores consistent with the measured properties of the samples of interest. However, conventional quantum methods are not able to accurately describe this system at the very high densities of interest and thus still cannot explain the high performance of the samples.

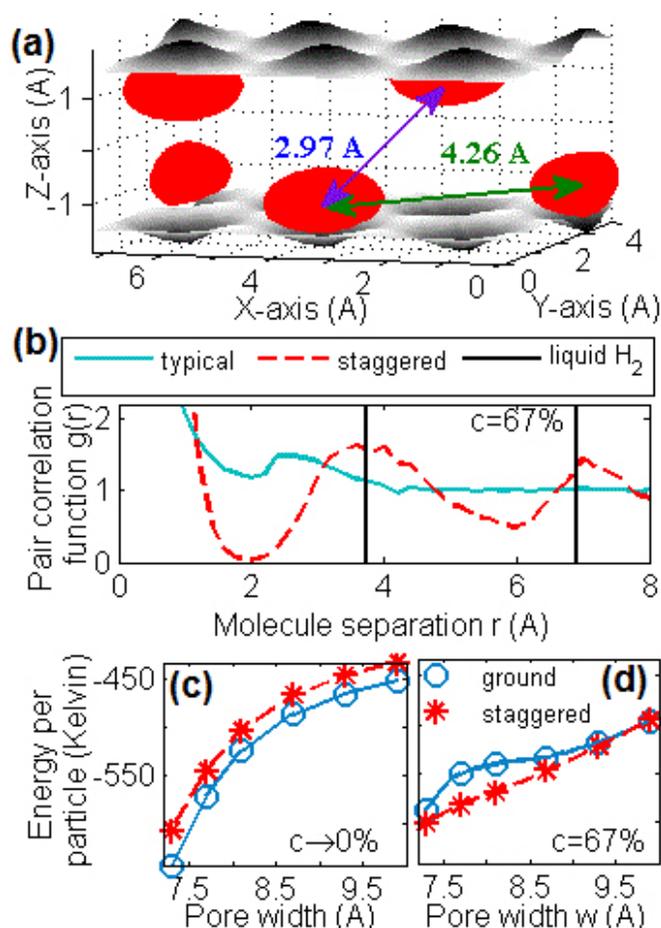


FIGURE 4. (a) Depiction of a "staggered" quantum state for H₂ adsorbed in a potential formed by two parallel layers of graphene, with 7.7 Å separation. The corrugated V=0 potential energy surfaces which enclose the adsorption volume are shown in gray. The red ovals within the pore show the regions of most concentrated probability density, where the H₂ is most likely to be found. Nearest neighbor distances between peaks in the probability density are also shown. (b) Pair correlation function for the staggered quantum state compared to a typical quantum state in the same pore. The pair correlation function gives the likelihood to find an H₂ a distance r away from another H₂, and is normalized to be equal to 1 for an ideal gas. The location of peaks in the pair correlation function for liquid H₂ are also marked [10]. (c) Energy of the staggered quantum state compared to the ground state (with zero kinetic energy) as a function of pore width for a coverage of $c=0\%$ and (d) $c=67\%$ of a full monolayer of adsorbed H₂.

CONCLUSIONS AND FUTURE DIRECTIONS

Because this project is nearly complete, there is not enough time to prove that H₂ storage targets can be met by utilizing the proposed quantum effect and understand its properties well enough to design new materials. Nevertheless, the necessary tasks to meet these goals are as follows,

- Typical BECs can be observed using deep-inelastic neutron scattering [11]. Preliminary deep-inelastic neutron scattering with the sample of interest is

consistent with the proposed BEC [4]. Specific heat measurements can also be done to prove the presence of a quantum effect.

- Probe the new physics of the system. In this novel BEC, particles condense into a state with non-zero kinetic energy, thus diffusion measurements of adsorbed H₂ [12] in the samples of interest using quasi-elastic neutron scattering may reveal how condensed particles move. Neutron diffraction measurements can also probe the positions of condensed particles relative to one another in the high density phase.
- Theoretically examine the link between the proposed BEC condensation and the observed high H₂ density. Classically, if we imagine the H₂ particles as hard spheres with a diameter of ~3.5 Å, there is an upper limit on their maximum density which is near the density of liquid H₂, and conventional quantum mechanics does not explain how this density can be exceeded. But the samples of interest do appear to exceed this upper limit. One may postulate that if the particles in this new BEC move relative to one another, and if they interact on a discrete time scale, then the system may achieve seemingly impossible high densities when any given pair of particles have a relative motion such that they only interact when they are farther apart than 3.5 Å, even though they may be closer together at other times. It is clearly possible for particles in this new BEC to move relative to one another, since they condense into a state with non-zero kinetic energy. Recent experimental work [13] has shown that electrons interact with their environment on a discrete time scale; this theory must now be extended to other particles, such as H₂ and particles in a BEC, and applied to the current system.

FY 2013 PUBLICATIONS

1. R.J. Olsen, M. Beckner, P. Pfeifer, M.B. Stone, C. Wexler, and H. Taub, “Quantum excitation spectrum of adsorbed hydrogen observed by inelastic neutron scattering,” *Carbon*, **58** 46-58 (2013).
2. C. Contescu, H. Zhang, R.J. Olsen, E. Mamontov, J.R. Morris & N. Gallego, “Isotope effect on adsorbed quantum phases: diffusion of H₂ and D₂ in nanoporous carbon,” *Physical Review Letters*, **110**, 236102 (2013).
3. J.R. Morris, C.I. Contescu, M.F. Chisholm, V.R. Cooper, J. Guo, L. He, Y. Ihm, E. Mamontov, Y.B. Melnichenko, R.J. Olsen, S.J. Pennycook, M. B. Stone, H. Zhang & N. C. Gallego, “Modern approaches to studying gas adsorption in nanoporous carbons,” *Journal of Materials Chemistry A*, DOI 10.1039/C3TA10701A (2013).
4. R.J. Olsen, “High temperature Bose condensation into an excited state at equilibrium,” *Physical Review Letters*, under review.
5. R.J. Olsen, M.B. Stone, “Coupling of rotational and vibrational motion to translational motion for H₂ adsorbed on corrugated graphite surfaces” *Physical Review B*, under review.

FY 2013 PRESENTATIONS

1. R.J. Olsen, “A high temperature Bose condensate of hydrogen molecules adsorbed in a narrow graphene pore” Carbon 2013 Conference, Rio de Janeiro Brazil, July 2013.
2. R.J. Olsen, “The quantum effects of pore structure on hydrogen adsorption,” 2013 Annual Merit Review, Washington, D.C., May 2013.
3. R.J. Olsen, DOE EERE Postdoctoral Research Awards Annual Meeting, “The quantum effects of pore structure on hydrogen adsorption,” Golden, CO, April 2013.
4. R.J. Olsen, “Quantum mechanics of hydrogen adsorption studied by neutron scattering”, University of Tennessee, Materials Science and Engineering, Knoxville TN, Nov. 2012.

REFERENCES

1. P. Pfeifer et al., 2010 DOE EERE Annual Merit Review Presentation, “multiply surface-functionalized nanoporous carbon for vehicular hydrogen storage,” (http://www.hydrogen.energy.gov/pdfs/review10/st019_pfeifer_2010_o_web.pdf).
2. R.J. Olsen, *Investigations of Novel Hydrogen Adsorption Phenomena* (PhD thesis), University of Missouri Columbia (2011).
3. P. Pfeifer et al., 2012 DOE BES Annual Progress Report, “New pathways and metrics for enhanced, reversible hydrogen storage in boron-doped carbon nanopores,” (http://www.hydrogen.energy.gov/pdfs/progress12/iv_h_7_pfeifer_2012.pdf).
4. R.J. Olsen, 2013 DOE EERE Annual Merit Review Presentation, “The quantum effects of pore structure on hydrogen adsorption,” (http://www.hydrogen.energy.gov/pdfs/review13/st107_olsen_2013_o.pdf).
5. R.J. Olsen, “High temperature Bose condensation into an excited state at equilibrium,” *Physical Review Letters*, under review.
6. R.J. Olsen & M.B. Stone, “Coupling of rotational and vibrational motion to translational motion for H₂ adsorbed on corrugated graphite surfaces” *Physical Review B*, under review.
7. R.J. Olsen et al., “Quantum excitation spectrum of adsorbed hydrogen observed by inelastic neutron scattering,” *Carbon*, **58**, 46-58 (2013).
8. P. Parilla et al., 2012 DOE EERE Annual Merit Review Presentation, “Hydrogen sorbent measurement qualification and characterization,” (http://www.hydrogen.energy.gov/pdfs/review12/st014_parilla_2012_o.pdf).
9. N. Gallego et al., “Hydrogen confinement in carbon nanopores: extreme densification at ambient temperature,” *Journal of the American Chemical Society* **133**, 13794 (2011).
10. M. Celli et al., “Microscopic structure factor of liquid hydrogen by neutron-diffraction measurements,” *Physical Review B* **71**, 014205 (2005).
11. S.O. Diallo et al., “Bose-Einstein Condensate in solid helium,” *Physical Review Letters* **98**, 205301 (2007).
12. C. Contescu et al., “Isotope effect on adsorbed quantum phases: diffusion of H₂ and D₂ in nanoporous carbon,” *Physical Review Letters*, **110**, 236102 (2013).

13. P. Catillon et al., “A search for the de Broglie particle internal clock by means of electron channeling,” *Foundations of Physics* **38**, 659 (2008).