

IV.H.7 New Pathways and Metrics for Enhanced, Reversible Hydrogen Storage in Boron-Doped Carbon Nanospaces

Peter Pfeifer, Ph.D (Primary Contact),
Carlos Wexler, Ph., M. Frederick Hawthorne, Ph.D.,
Mark W. Lee, Ph.D., Satish S. Jalistegi, Ph.D.

The Curators of the University of Missouri
Office of Sponsored Program Administration
University of Missouri
310 Jesse Hall
Columbia, MO 65211
Phone: (573) 882-2335
Email: PfeiferP@missouri.edu

DOE Program Officer: Bonnie Gersten
Phone: (301) 903-0002
Email: Bonnie.Gersten@science.doe.gov

Subcontractors:

- Ping Yu, Ph.D., University of Missouri
- Haskell Taub, Ph.D., University of Missouri
- Anupam Sing, Ph.D., University of Missouri
- Jan Ilavsky, Ph.D., Argonne National Laboratory
- Bogdan Kuchta, Ph.D., Univ. Aix-Marseille, France
- Lucyna Firlej, Ph.D., Univ. Montpellier 2, France
- Raina Olsen, Ph.D., Oak Ridge National Laboratory

Objectives

- An integrated synthesis/characterization/computational effort to develop novel materials: monolithic boron-doped carbon made from polymeric precursors, crisscrossed by networks of nanopores.
- To develop a fundamental understanding of the mechanisms by which boron, through its electron-deficient electronic structure and long-range effect on distant carbon atoms, combined with appropriate pore geometries, creates deep potential wells which can hold films of physisorbed molecular hydrogen at densities much higher than undoped carbon.
- Such high-density films and their understanding at the molecular, statistical mechanical, and macroscopic thermodynamic level are critical for the rational design of high-performance materials with controlled reversible storage characteristics at low pressure and room temperature.

Abstract, Progress Report and Future Directions

Carbon-based materials have recently shown promise for hydrogen storage at moderate pressures. Our group

has focused on the development of materials derived from synthetic precursors in order to optimize, measure and control pore geometries at the sub-nm scale; and to enhance the adsorption of H₂ (particularly at low pressure, high temperature) by increasing the depth of the H₂-carbon potential by chemically functionalizing the adsorbent's surface. Our group has spearheaded the effort to improve these materials and in previous grant periods have reported: (i) record-breaking H₂ storage in very high-surface area activated carbons; (ii) *ab initio* theoretical predictions that boron doping of carbon at 5-10% B:C concentration raises the H₂ binding energy from ~5 kJ/mol to 10-14 kJ/mol; (iii) Grand Canonical Monte Carlo (GCMC) simulations that successfully reproduce the experimental adsorption of H₂ in heterogeneous pore structures, and that demonstrated enhanced H₂ storage in B-doped carbon; (iv) demonstrated experimentally the existence of B-C bonds in B-doped carbon; (v) demonstrated experimentally that in B-doped carbons the isosteric heat of adsorption nearly doubles from 5-7 kJ/mol to 9-12 kJ/mol, this is accompanied by an enhancement of the H₂ sorption at cryogenic and room temperature; (vi) demonstrated that activated carbon from synthetic precursors have a nearly monodisperse network of narrow pores; (vii) developed pore characterization methods based on small-angle X-ray scattering (SAXS); and (viii) developed the theoretical background to utilize incoherent inelastic neutron scattering (IINS) off adsorbed H₂ to characterize the interaction potentials as seen by molecular H₂ in sub-nm pores. In what follows we present the most relevant results attained in the current reporting period.

a) Observation of anomalous adsorption of H₂ in synthetic carbon: significantly higher excess adsorptions normalized per Brunauer-Emmett-Teller (BET) surface area at both cryogenic and room temperature (e.g., at room temperature synthetic sample HS:0B has more than doubles the performance of our best lignocellulose carbon, sample 3K). This indicates higher binding energies (consistent with a narrower pores). In addition, synthetic carbons show anomalous excess adsorption isotherms, with the maximum of the excess adsorption occurring at higher than normal pressures. See Figure 1.

b) Determination of adsorbed film characteristics: we succeeded in measuring important adsorbed film characteristics (excess and absolute adsorption, isosteric heat of adsorption, film thickness and volume, saturation density) by using an integrated combination of experimental methods (N₂ characterization, He "picnometry", H₂ adsorption isotherms at cryogenic and room temperature up to 200 bar, SAXS), data processing (extrapolation to calculate saturated

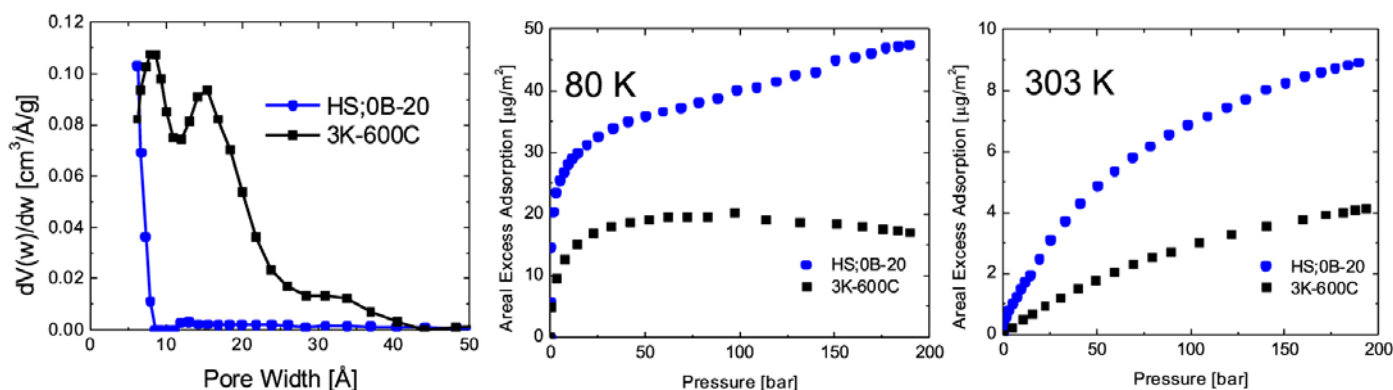


FIGURE 1. Pore size distribution (left), and H₂ excess adsorption per unit area at 80 K (center) and 303 K (right) for synthetic carbon HS;0B ($\Sigma_{\text{BET}} = 900 \text{ m}^2/\text{g}$) and lignocellulose carbon 3K ($\Sigma_{\text{BET}} = 2,600 \text{ m}^2/\text{g}$).

film density), theoretical modeling (isosteric heats from Clausius-Clapeyron eq., absolute adsorption, film thickness from monotonicity of isosteric heat), and computational efforts (GCMC). Film densities are significantly in excess of the density of liquid H₂. See Figure 2.

c) Design and construction of sub- and super-critical H₂ Sievert instrument: we have built a Sievert sorption instrument to be used for sub-critical and super-critical H₂ adsorption (temperature range: 4-300+ K). This will permit determination of BET surface areas, and pore and skeletal volumes using H₂ rather than N₂; and permit a more precise determination of adsorbed film densities, especially in synthetic precursors that have maximum of the excess adsorption at anomalously high pressures.

d) High resolution transmission electron microscopy: Aberration corrected scanning transmission electron microscopy performed at the Oak Ridge National Laboratory (ORNL) Center for Nanophase Materials Sciences show detailed atomic structure of synthetic carbon: these have

regions of graphitic and amorphous carbon consistent with $700 \text{ m}^2/\text{g}$ BET surface areas. See Figure 2.

e) IINS: we conducted experiments at ORNL over an unprecedented broad range of energy and momentum transfer. We developed a novel theoretical methodology that permitted the classification of the H₂ excitations into localized and mobile states. This provides a measure of the planarity of the adsorption surface on the >1 nm scale, and gives insight on the quantum states of adsorbed H₂.

f) Pore conformability: we have performed a mechanical analysis of the stability of pores in carbon, this indicates that pores with lateral (in plane) dimensions larger than 2-4 nm would naturally collapse and close, consistent with our SAXS experiments. More interestingly, we observe that pores that are above this “critical length” may be partially opened by H₂ at $P > 20\text{-}30$ bar. Interestingly, this model results in excess adsorption isotherms that do not show a clear maximum at low and moderate pressures.

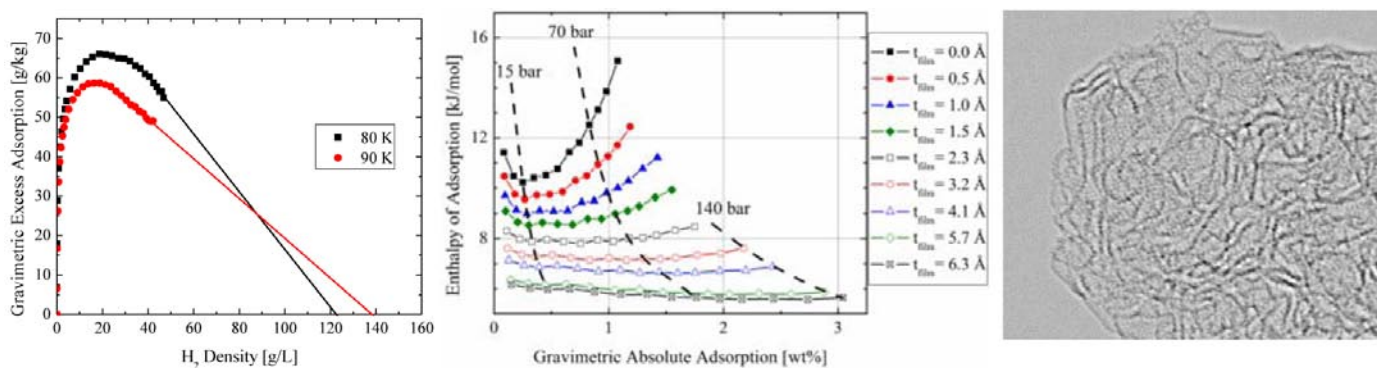


FIGURE 2. Determination of saturated film densities from extrapolation of the excess adsorption (left). Determination of film thicknesses (and volume) from the thermodynamic requirement that the isosteric heat of adsorption is a monotonically decreasing function of coverage (center). At the lower bound for film thickness, $t_{\text{film}} = 4.1 \text{ Å}$, these results are consistent with the adsorption values (Figure 1). High resolution transmission electron microscopy of synthetic carbon HS;0B (right).

Publications (including patents) acknowledging the grant or contract

Publications Acknowledging DOE-BES Support during FY 2012

1. *The Quantum Excitation Spectrum of Adsorbed Hydrogen*, R. Olsen, M. Beckner, P. Pfeifer, C. Wexler, and H. Taub, Phys. Rev. Lett. (under review).
2. *Functional B-C Bonds in Nanoporous Boron Carbide and Boron Doped Carbon Materials*, J. Romanos, D. Stalla, M. Beckner, A. Tekeci, G. Suppes, S. Jalisatgi, M. Lee, F. Hawthorne, D. Robertson, L. Firlej, B. Kuchta, C. Wexler, P. Yu, P. Pfeifer, Carbon (under review).
3. *Elastic Pore Structure of Activated Carbon*, M.J. Connolly and C. Wexler, Phys. Rev. B (in preparation).
4. *Infrared Study of Boron-Carbon Chemical Bonds in Boron Doped Activated Carbon*, J. Romanos, M. Beckner, D. Stalla, A. Tekeci, G. Suppes, S. Jalisatgi, M. Lee, F. Hawthorne, J.D. Robertson, L. Firlej, B. Kuchta, C. Wexler, P. Yu, and P. Pfeifer (in preparation).
5. *Hydrogen Adsorption Studies of Engineered and Chemically Modified Activated Carbons*, M. Beckner, Ph.D. Thesis (University of Missouri, 2012, director: P. Pfeifer).
6. *Nanospace Engineering of Porous Carbon For Gas Storage*, J. Romanos, Ph.D. Thesis (University of Missouri, 2012, director: P. Pfeifer).
7. *Numerical Analysis of Hydrogen Storage in Carbon Nanopores*, C. Wexler, R. Olsen, P. Pfeifer, B. Kuchta, L. Firlej, Sz. Roszak, in *Condensed Matter Theories* Vol. 25, Eds. E.V. Ludeña, R.F. Bishop, & P. Iza (Nova Science Publishers, 2011).
8. Sub-nanometer characterization of activated carbon by inelastic neutron scattering, R. Olsen, L. Firlej, B. Kuchta, H. Taub, P. Pfeifer, and C. Wexler, Carbon **49**, 1663-1671 (2011).

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1. *Conformability of Pores in Activated Carbon*, M. Connolly and C. Wexler, 1st Iberoamerican Symposium on Adsorption, Recife, Brasil, May, 2012.
2. *Elastic Pore Structure of Activated Carbon*, M. Connolly and C. Wexler, The 6th International Workshop on Characterization of Porous Materials—from Angstroms to Millimeters (CPM-6), Delray Beach, FL, April, 2012.

3. *Recoiling and Bound Quantum Excitations of Adsorbed Hydrogen As An Assessment of Planarity*, R. Olsen, H. Taub and C. Wexler, The 6th International Workshop on Characterization of Porous Materials—from Angstroms to Millimeters (CPM-6), Delray Beach, FL, April, 2012.
4. *Reversible Storage of Hydrogen and Natural Gas in Nanospace-Engineered Activated Carbons*, J. Romanos, M. Beckner, T. Rash, P. Yu, G. Suppes, and P. Pfeifer, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, W33.05 (2012))*, Boston, MA, March 2012.
5. *Measured Enthalpies of Adsorption of Boron-Doped Activated Carbons*, M. Beckner, J. Romanos, E. Dohnke, A. Singh, J. Schaeperkoetter, D. Stalla, J. Burress, S. Jalisatgi, G. Suppes, M. F. Hawthorne, P. Yu, C. Wexler, and P. Pfeifer, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, W33.07 (2012))*, Boston, MA, March 2012.
6. *Performance of Carbon Hydrogen Storage Materials as a Function of Post-Production Thermal Treatment*, E. Dohnke, J. Romanos, M. Beckner, J. Burress, P. Yu, and P. Pfeifer, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, W33.08 (2012))*, Boston, MA, March 2012.
7. *The Stationary States of Adsorbed Hydrogen*, R. Olsen, H. Taub, and C. Wexler, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, W33.06 (2012))*, Boston, MA, March 2012.
8. *Measured Enthalpies of Adsorption of Boron-Doped Activated Carbons*, M. Beckner, J. Romanos, E. Dohnke, A. Singh, J. Schaeperkoetter, D. Stalla, J. Burress, S. Jalisatgi, G. Suppes, M.F. Hawthorne, P. Yu, C. Wexler, and P. Pfeifer, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, W33.07 (2012))*, Boston, MA, March 2012.
9. *Adsorption-induced Pore Expansion and Contraction in Activated Carbon*, M. Connolly and C. Wexler, *March 2012 Meeting of the American Physical Society (Bull. Am. Phys. Soc. 57, X11.11 (2012))*, Boston, MA, March 2012.
10. *Nanoporous Carbon for Reversible Storage of Hydrogen*, C. Wexler, Low Carbon Earth Summit-2011 (LCES-2011), Dalian, China, October 2011.