

IV.C.1h Advanced Boron and Metal-Loaded High Porosity Carbons

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- In collaboration with NIST (neutron scattering) we observed that the inclusion of boron into the sp²-bonded carbon structure produces a local enhancement in the H₂ binding energy (used boron-substituted carbon nanotubes, see Figure 2).

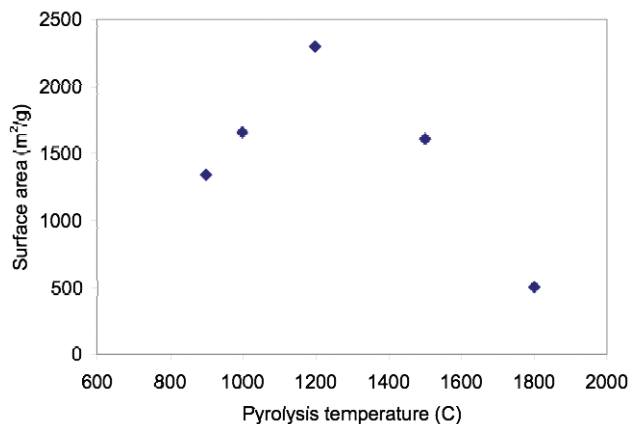


FIGURE 1. SSA of activated carbon as a function of pyrolysis temperature of polyfurfuryl alcohol/polyethylene glycol diacid blend precursors. Data shows importance of processing temperature on the SSA with a pronounced maximum at 1,200°C.

Partner Approach

Penn State is developing new high surface area carbon materials with enhanced hydrogen binding energy. This will be accomplished by chemical substitution of boron into the hexagonal sp² carbon framework and atomic dispersion of metal atoms bound to the boro-carbon structure. These new boro-carbon materials are synthesized in high temperature plasmas (e.g., generated by a feedback-stabilized electric arc), by pyrolysis of boron-carbon precursor molecules and by post synthesis insertion of boron into high specific surface area (SSA) carbons. We will measure the physical properties, local chemistry and pore structure of these H₂-storage materials and attempt to correlate them with H₂ storage performance at various pressures and temperatures.

Partner FY 2006 Results

- Devised three synthesis tracks that produce Boron-substituted high surface area carbons: High-T plasma, pyrolysis of B-containing organic and polymeric precursors, modification of high SSA carbons via tetraethyl ammonium borohydride (TEAB)...all incorporate B in the sp² structure (see Figure 1).

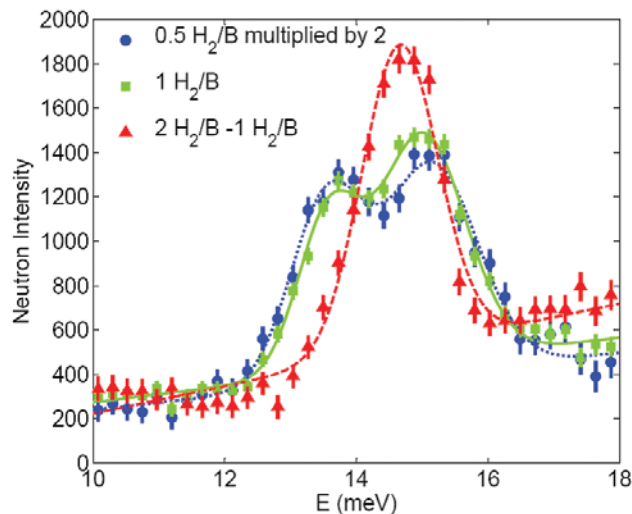


FIGURE 2. Inelastic neutron spectra vs temperature for rotational transitions of hydrogen adsorbed on boron-doped (1%) single-walled carbon nanotubes. The spectrum evolves from a singlet to a doublet with increasing temperature. The former (singlet) is associated with hydrogen bound to pristine sp² hexagons, while the latter (doublet) is identified with hydrogen bound to a B-doped hexagon. The doublet survives at high temperature, thus demonstrating the higher energy for hydrogen bound to the B-doped carbon hexagon.

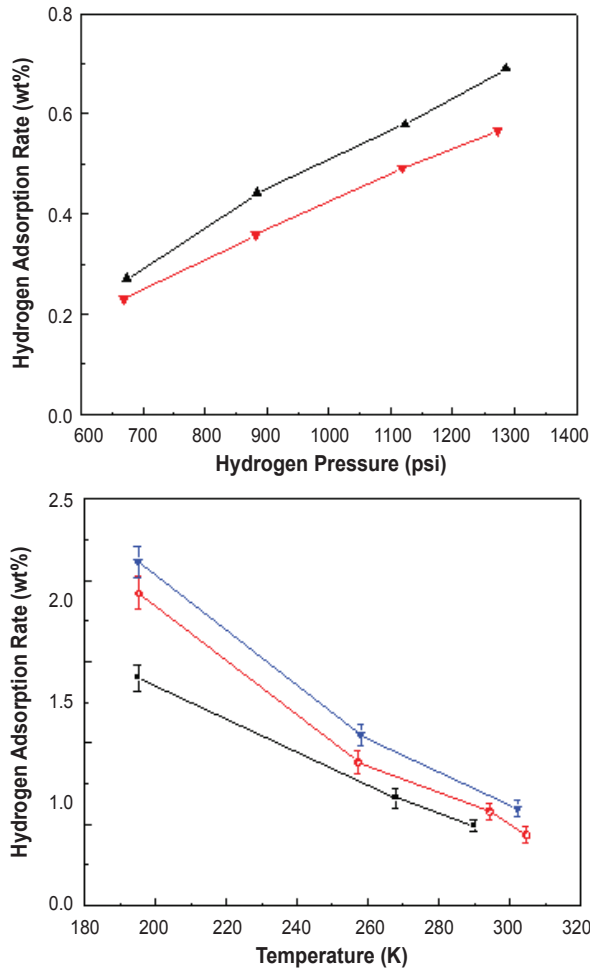


FIGURE 3. (top) Hydrogen adsorption isotherms on both phenylacetylene (PA) and phenyldiacetylene (PDA) based B/C materials at 23°C. Each hydrogen uptake is completely reproducible in the repeating adsorption-desorption cycles. The PDA based B/C material, with higher B content and surface area, consistently shows a higher level of hydrogen adsorption than PA-based B/C material. About 0.7 wt% hydrogen absorption is achieved at ambient temperature under 1,300 psi hydrogen pressure. This suggests that the substituted B elements may enhance hydrogen adsorption at ambient temperature. The bottom graph shows the effect of temperature on hydrogen adsorption on B/C (PDA-2-b) material under 900, 1,100, and 1,300 psi hydrogen pressure, respectively.

- Initial results suggest that boron may enhanced room temperature hydrogen storage in boro-carbons (see Figure 3).
- Investigated and established the experimental correlation of stored electronic charge with hydrogen storage in one class of our materials. This appears to be a time-efficient means to screen new materials (see Figure 4).

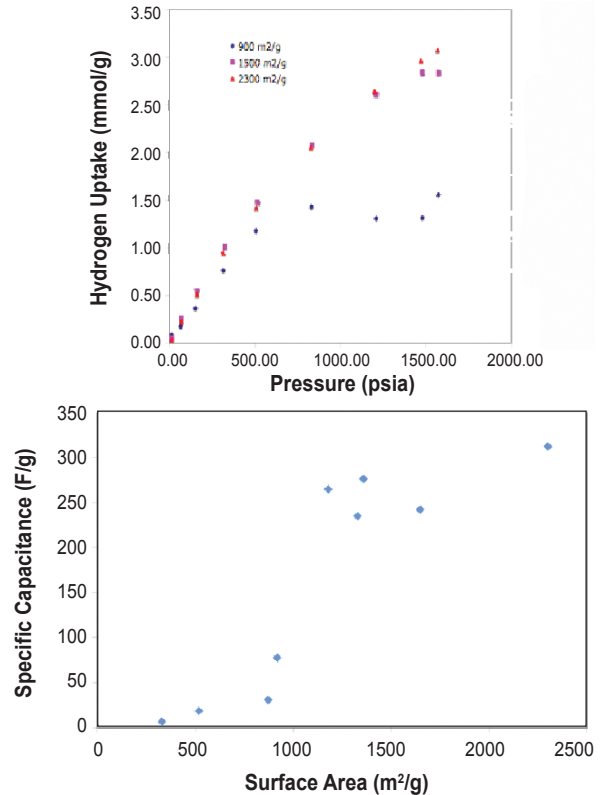


FIGURE 4. (top) Hydrogen uptake as a function of pressure and (bottom) double layer capacitance as a function of surface area of the activated carbons produced by the pyrolysis of blends of polyfurfuryl alcohol/polyethylene glycol diacid under inert atmosphere at 900°C. Note the correlation of hydrogen storage and double layer capacitance. The latter is a facile, table-top measurement which could serve as a quick screen for promising hydrogen storage carbon and boro-carbon materials.

- Observed two H₂ binding sites via nuclear magnetic resonance (NMR) in B-substituted carbons (see Figure 5).
- Designed, built and tested an automatic *differential* volumetric H₂ storage apparatus for evaluating small size samples (~10-50 mg) in the temperature range ~-200 to +400°C and at pressures from ~0 to 100 atm.
- Calculated in the local density approximation, the energetics of boron incorporated into a graphene lattice it was found that boron does not prefer to cluster even at very high concentrations (B:C;1:3). (see Figure 6)
- Calculated in the LDA approximation that boron incorporation in the graphene lattice stabilizes the atomic dispersion of metal (M) near the boron sites (see Figure 6).

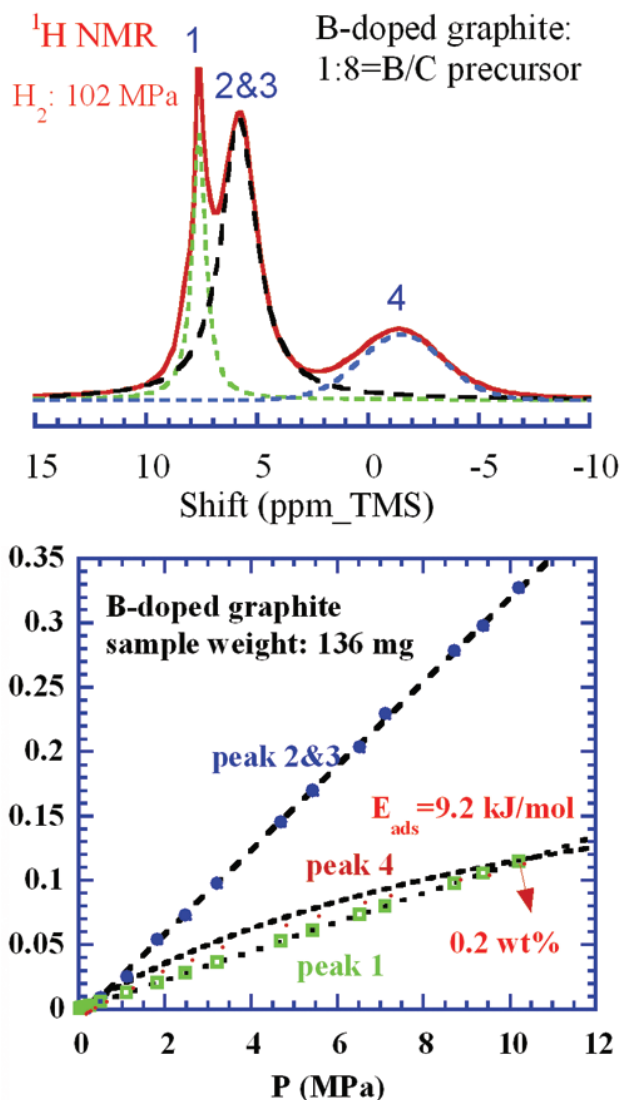


FIGURE 5. NMR results on PDA B/Carbons, e.g., PDA-2-b sample examined by a high pressure ^1H NMR instrument under hydrogen pressure of 102 MPa (at UNS Professor Wu's laboratory) (top) shows three NMR peaks. Peak 1 is associated with hydrogen gas in a capillary inserted inside the NMR sample tube as an intensity standard. Peak 2 is associated with desorbed free gas molecules in the sample space as well as adsorbed gas molecules on the external surfaces of particulates and grains of the powdered sample. The fact that the adsorbed and desorbed gas molecules are not distinguishable is due to the rapid exchanges caused by fast adsorption and desorption over the timescale of NMR. Peak 3 is associated with adsorbed molecules in confined spaces where exchange with desorbed gas molecules are spatially restricted. The bottom graph shows peak intensities of the ^1H NMR spectrum as functions of pressure for a 136 mg B-doped graphite sample.

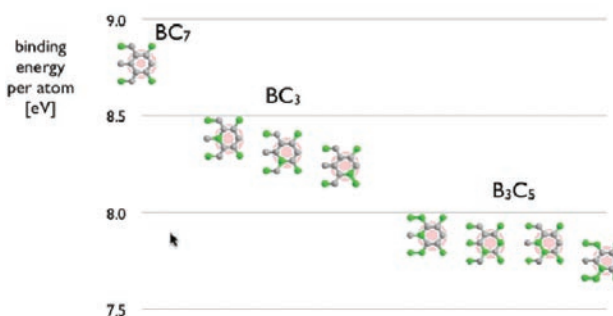


FIGURE 6. Preferred geometries calculated for boron doping across a range of concentrations. Through first-principles calculations of structural energetics, we have determined both the optimal locations for boron atoms within a graphitic sheet (shown above) and the deposition and atomic dispersion energies for metal atoms placed in contact with the electron-deficient boron-doped graphene sheet. Calculations are performed with density functional theory in the pseudopotential approximation with a plane-wave basis to treat period systems and localized bases for certain non-periodic discrete molecular systems. Ultrasoft pseudopotentials of the Vanderbilt type are used for computational efficiency, which is especially important for systems with strong potentials such as carbon and the light transitions metals. Our calculated binding energies of hydrogen to these structures range from 0.1 to 1.0 eV, with several plausible geometries falling in the neighborhood of ~ 0.3 eV, the ideal range for reversible room temperature hydrogen storage. Experimentally, doping at the B:C;1:3 level has already been demonstrated in the literature.

Partner FY 2007 Plans

In the previous year, we demonstrated that our synthesis approaches to produce high surface area materials with high boron content are working well. We have shown that boron substitution into the sp^2 lattice produces an increased binding energy for H_2 as seen in NMR, inelastic neutron scattering and H_2 storage experiments. In the following fiscal year, we will intensify our efforts to increase the boron level in our boron-carbon materials and focus on understanding the pore structure-local chemistry-H-storage relationship. We also plan to disperse low-Z metals in our high SSA materials that may be atomically stabilized via boron-binding. H-storage isotherm measurements will be performed on these materials. We will continue to cooperate with our CoE partners particularly at Air Products, NREL and NIST.

FY 2006 Publications/Presentations

1. Freedom Car Tech Team meeting, March 2006, Washington, D.C.
2. DOE Annual Merit Review, May 2006, Arlington, VA.