

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

Vincent Crespi (Primary Contact), Peter Eklund, T. C. Mike Chung, and Henry C. Foley

The Pennsylvania State University
Eberly College of Science
104 Davey Laboratory, MB193
University Park, PA 16802
Phone: (814) 863-0163; Fax: (814) 865-3604
E-mail: DOE_H2.20.ipserc@spangourmet.com

DOE Technology Development Manager:
Carole Read

Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-05O15077

Project Start Date: February 1, 2005
Project End Date: January 31, 2010

- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of the hydrogen-substrate interaction to develop a novel class of highly electron deficient carbon frameworks, and a subclass thereof with light metal atoms dispersed on the same framework. In the past year we have successfully demonstrated a substantial enhancement in the interaction of hydrogen with this modified surface, including experimental demonstration of hydrogen physisorption at energies substantially larger than those of traditional sorbents. The target adsorption energy is in the range of 15-30 KJ/mol. We have doubled the adsorption energy from 4-6 to 10-12 KJ/mol and have plans in place for further increases. We are on track to develop sorbents that can meet the DOE 2015 hydrogen storage targets for gravimetric and volumetric storage densities at reasonable cost in a reversible system, although further breakthroughs in synthesis will be necessary to increase boron content, tune local geometries, maintain and increase porosity, and obtain optimal properties in a homogeneous fashion.

Accomplishments

- The binding energy for hydrogen as measured by isosteric heats of adsorption has been increased to 10-12 KJ/mol, much higher than in conventional activated carbons (4-6 KJ/mol), for two distinct synthetic routes. These values are approximately 50% larger than the confirmed values from the previous year, and begin to approach those necessary for high capacity reversible room-temperature hydrogen storage (15-30 KJ/mol).
- Synthesis of B-doped nanoporous carbons with high surface area ($>1,000 \text{ m}^2/\text{g}$) and large pore volumes (0.8 cc/g) by pyrolysis of tetraethylammonium borohydride containing polyfurfuryl alcohol and CO_2 activation, an improvement of 200% in surface area over a year previous.
- CO_2 activation selectively removes carbon, leaving behind boron-enriched nanoporous material. This may provide a straightforward, low-cost route to increased effective boron doping.
- The storage capacity of boron-doped nanoporous carbon (at 5 wt% boron) with surface area between

Objectives

- Identify a new class of high surface area boro-carbon and metal boro-carbon material systems with surface chemistry tuned for a stronger hydrogen binding interaction that will enable 2015 DOE target volumetric and gravimetric reversible hydrogen storage capacity, through a synergistic combination of materials synthesis, characterization and first-principles computation.
- Synthesize highly porous boro-carbons and metal boro-carbons with simultaneous ultra-high boron content, high surface area and tunable curvature.
- Enhance the stability of highly dispersed metals on carbon frameworks, including atomic-level dispersion that is stable against aggregation.
- Maintain these properties in a system with low-to-moderate economic cost of raw materials and stability over many cycles.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and volume
- (B) System Cost

1,000–1,500 m²/g was 0.5 wt% at room temperature and 100 bars. We have synthetic routes in hand to reach 10 wt% boron, and are making substantial progress in developing increased surface areas at higher B concentrations. Since binding energy is a strong function of sheet curvature, greater room-temperature adsorption can be obtained by optimizing curvature.

- First principles computations have identified model systems with hydrogen binding energies of 30 KJ/mol in light-weight frameworks designed to be resistant to aggregation. Experimental synthetic efforts on metal boro-carbons are beginning to bear fruit.



Introduction

A new class of hydrogen sorbents with substantially enhanced hydrogen binding energies in a low-mass framework shows potential to meet DOE gravimetric targets, with further optimization. The introduction of boron into a curved high surface area carbon framework induces electron deficiency in the framework and so increases the propensity to bind H₂ reversibly at energies intermediate between traditional physical and chemical adsorption. Additionally, we have demonstrated through first principles calculations, taking place in concert with arc synthesis, that this same electron deficiency can help stabilize the atomic dispersion of light metal atoms. The exposed orbitals of these atoms then provide another venue for new binding chemistry, importantly, in a geometry that is naturally resistant to aggregation due to the continuous rigid nature of the porous framework. We also continue to develop an improved means to control porosity and activate surface area in heavily boron-doped carbons.

Approach

Our approach is to intimately couple the synthetic, computational and characterization efforts locally at Penn State with the world-leading characterization tools (and also synthetic and computational efforts) available throughout the center to break new ground in the discovery of new materials systems that modify the binding chemistry towards hydrogen at a fundamental level by controlling electron content in a rigid framework. The starting point, a carbon-based nanoporous framework, provides a robust, lightweight, high surface area, mechanically rigid, low-cost system with the structural cohesiveness to withstand the substantial variations in local chemistry that are necessary to induce enhanced hydrogen adsorption. These modifications include withdrawing substantial

numbers of electrons from the structure, dispersing exposed metal atoms onto the structure, and forcing topologically or topographically frustrated geometries that have the potential to generate very large local electric fields and open-shell configurations. Each of these final states - electron deficiency, exposed uncompensated orbitals and local fields - provides a distinct fundamental means to generate new classes of adsorptive interaction that is intermediate between traditional chemical and physical adsorption and in the optimal range for reversible room-temperature hydrogen storage. In all stages of this process careful attention is paid to DOE goals in materials cost, volumetric and gravimetric density, and stability over multiple cycles.

Results

A new synthesis route has been developed to prepare boron substituted carbon (B/C) materials that show a significantly higher hydrogen binding energy and physisorption capacity, compared with the corresponding carbonaceous materials. The chemistry involves a pyrolysis of the designed boron-containing polymeric precursors, which are the polyaddition adducts of phenylene diacetylene (with and without lithiation) and BCl₃. During pyrolysis, most of the boron moieties were transformed into a B-substituted graphitic structure, and the *in situ* formed LiCl and HCl by-products created a micro-porous structure. Micro-porous B/C material with B content >7% and surface area >800 m²/g shows hydrogen physisorption capacity 0.7 and 2.65 wt% at 300 and 77 K, respectively, under 350 psi hydrogen pressure. Adsorption-desorption cycles were repeated many times without detectable changes. Adsorption isotherm and *in situ* ¹H nuclear magnetic resonance (NMR) studies, indicate a binding energy of about 10-12 kJ/mol hydrogen, significantly higher than the 4-6 kJ/mole reported on most graphitic surfaces. The conjugated ethylene-phenyl (I) or acetylene-phenyl (II) moieties (Figure 1), with B atoms in the polymer backbone increase B-C bond strength and enhance the carbonization conversion. The facile B-Cl side groups involve inter- and intra-molecular (cyclization), essential in the thermal transformation process into a graphitic structure.

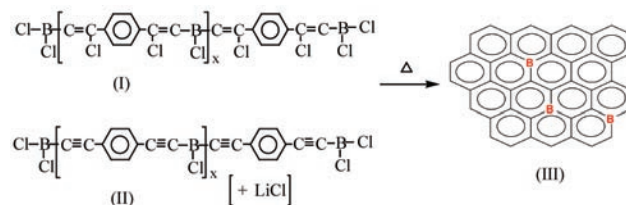


FIGURE 1. Synthesis of B/C Materials using B-Containing Precursors

For enhanced H_2 physisorption it is very important to obtain micro-porous B/C material with a high surface area. Precursor (I) creates a small surface area, possibly due to evolution of HCl and BCl_3 during solid-state transformation. In precursor (II), $LiCl$ molecules were formed during the polycondensation and were maintained during pyrolysis, $LiCl$ being removed from the B/C product by water washing. Evidentially, the impregnated $LiCl$ offers an effective means to obtain micro-porous B/C material with a high surface area. The porous size distribution has a narrow peak centered at 3.5 nm pore diameter and a small shoulder extending to atomic-scale pores. B-N complexization with trialkylamine at ambient temperature indicates that one-third of the B sites interact with trialkylamine. The complexes were dissociated after heating $>300^\circ C$ to regenerate the original B/C material with almost the same weight and surface area.

Figure 2 shows hydrogen adsorption at 293, 203, and 77 K under various pressures. The hydrogen uptake is almost linear in the hydrogen pressure, unlike carbon materials which reach a saturation level in relatively low pressure. About 0.7 wt% hydrogen adsorption was observed at ambient temperature under 350 psi H_2 pressure; this wt% is about 50% higher than those of carbonaceous materials with similar surface areas. At 77 K, hydrogen adsorption reaches the 2.65 wt%. Evidently, the substituted boron is essential to enhancing hydrogen adsorption. The H_2 binding energy was estimated by adsorption isotherms (at 77 and 87 K) under low hydrogen pressure (<1 bar) in Figure 3. The resulting initial isosteric heat of adsorption for B/C material is 12.5 kJ/mol and maintains quite a high adsorption energy level to higher surface coverage (10.8 kJ/mol for 0.62 wt% H_2 uptake). These are significantly higher than those observed in the undoped and some metal doped carbonaceous materials.

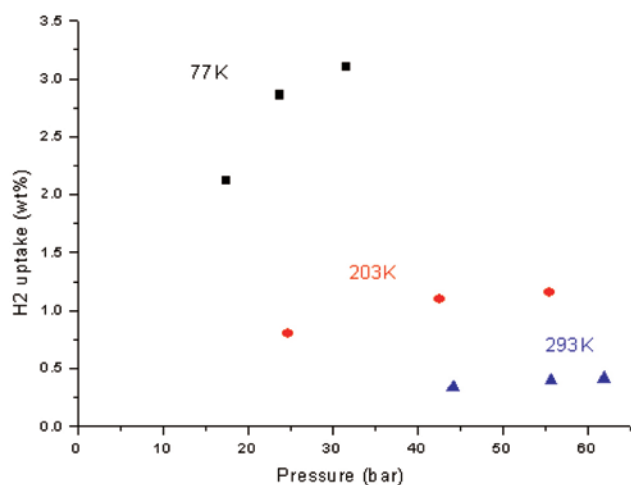


FIGURE 2. Hydrogen Adsorption vs. Pressure at 77, 203, and 293 K for a Sample with 7.2 wt% B Content and 800 m^2/g Surface Area

We have also used controlled CO_2 activation of samples produced by pyrolysis of a mixture of tetraethylammonium borohydride (TEAB), polyethylene glycol (pore former), and furfuryl alcohol/polyfurfuryl alcohol (FA) to produce boro-carbons across a range of pore volumes and surface areas. The pore size distribution was measured using methyl chloride adsorption. CO_2 activation of this nanoporous boro-carbon selectively removes carbon, leaving a high surface area sample enriched with boron. Samples with FA: TEAB molar ratios (1:0.5) and (1:1) show increasing pore volume at shorter activation times (<3 hours) with a narrow pore size distribution of 0.6-1 nm and a nanopore volume of 0.70-0.87 cc/g. When activated beyond 3 hours, the pore volume decreases, eventually reaching pre-activation levels as boron catalyzes graphitization. A hydrogen binding energy of 9.5 kJ/mol was extracted from adsorption isotherms at 0, 20 and $40^\circ C$ (at APCL), much higher on conventional activated carbons (4-6 kJ/mol). The binding energy of a higher boron content sample is currently being measured. Samples reversibly adsorbed hydrogen with maximum uptake of 0.47 wt% at room temperature and 100 bar pressure and 1.33 wt% at 77 K and 1 atm. The improvement in room temperature storage, at even this relatively low boron concentration, bodes well for further optimization.

We further established that B can be reliably incorporated substitutionally into the wall of single-walled nanotubes (SWNT), as a well-ordered test-bed material, by Raman scattering, scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS), optical absorption, neutron activation analysis at the National Institute of Standards and Technology, and sheet resistance of percolated SWNT films. Boron content correlates with D-band scattering, indicating that while high-T vacuum annealing removes

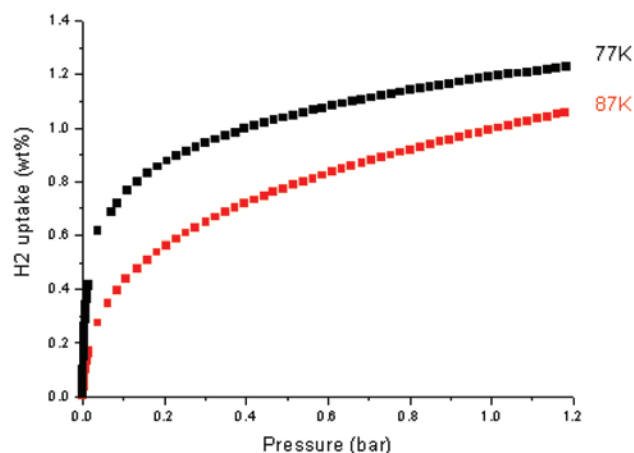


FIGURE 3. Absorption Isotherms for a Sample with 7.2 wt% B Content and 800 m^2/g Surface Area

wall damage in the acid-treated tubes, it cannot remove D-band scattering from B substitution (Figure 4). A new feature in the optical absorption at 0.4 eV is apparently associated with transitions between hybridized states in the impurity band and the van Hove singularity at the top of the valence band. Since it is difficult to exceed 1-2 at% B while maintaining sp^2 hybridization when B is incorporated into the electrode, we also exposed samples to B_2O_3 under flowing ammonia at 0.3-1.0 atm at $700 < T < 900^\circ\text{C}$. EELS experiments and neutron activation showed 5 at% B. Amorphous sp^2 carbons are even hungrier for boron: under the same reaction conditions B-doping was two times higher in amorphous sp^2 carbons than in ordered SWNT walls. This reaction should be applicable to B-doping a variety of nanocarbons.

To produce large-scale quantities of high surface area metal-doped boro-carbons, we used arc discharge to form nanoparticulate metalborocarbides and subsequently transformed these carbides into porous carbons via high temperature treatment in flowing chlorine. This is similar to processing used for carbide-derived-carbons. We establish non-equilibrium reaction conditions that leave behind a controlled small amount of metal and boron in a porous sp^2 structure. Small (20 nm) AlB-carbide nanoparticles were prepared from aluminum-boron-loaded carbon electrodes, at 50 grams per hour. We see no obstacles in making other nano-metal boro-carbides with Mg, Ca, etc. Converting the carbide to sp^2 while retaining metal and boron is challenging because the reaction rates at the nanoscale are much faster than for micron or bulk carbide-derived carbons. The process produces small graphitic shells comparable in diameter (10 nm) to the starting carbide nanoparticles and larger graphitic shells (~50 nm diameter) in a clear bimodal distribution (Figure 5).

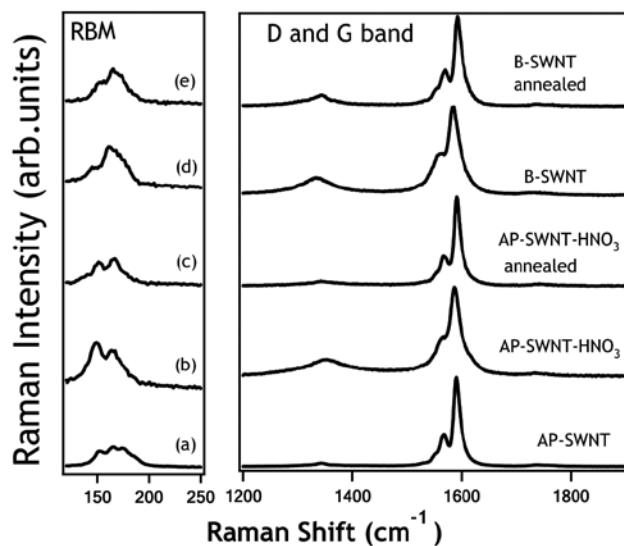


FIGURE 4. Raman Spectra of B_2O_3 Processed Nanotubes

EELS and energy dispersive spectroscopy (EDS) analysis revealed a residual B and Al content of 5 at% and ~1 at%, indicating that Al-Cl reaction kinetics are faster than B under these conditions. Further experiments are being performed at lower temperatures and different concentrations of Cl_2 .

We have also computed binding energies and optimal boron locations within archetypal three-dimensional nanoporous geometries that model the nanoporous boro-carbons, both with and without metal dopants. Our first-principles calculations establish that these structures can show enhanced binding of H_2 , with curvature playing a critical role, as it does for nanotube geometries, and consistent with our experimental results on enhanced binding to boron-doped carbons described above. The combination of heptagons, negative Gaussian curvature and pore size can induce binding at 0.14 eV/molecule (Figure 6). We have also expanded

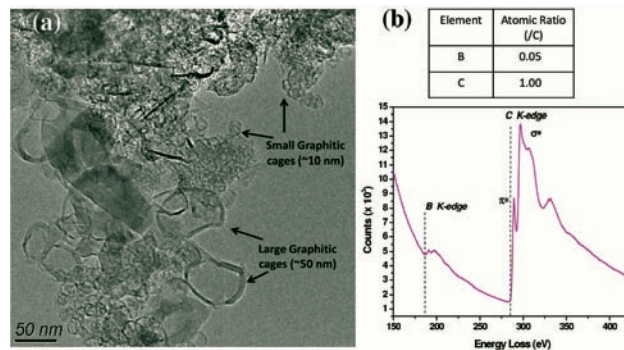


FIGURE 5. Results of a 2.5 h Cl_2 Gas Treatment @ $T = 600^\circ\text{C}$ and $P = 1$ atm for Boro-Carbides

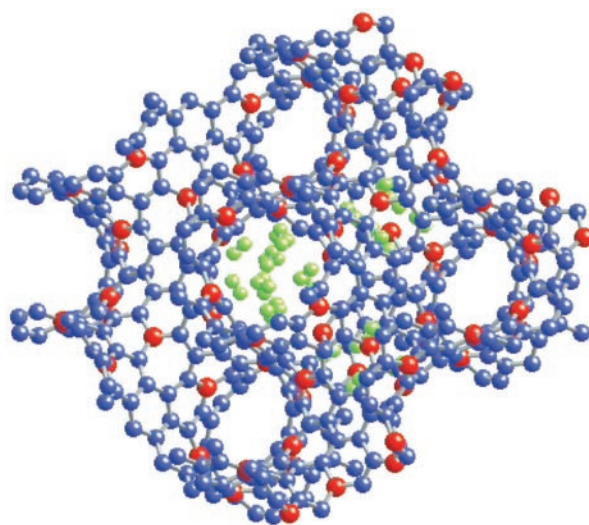


FIGURE 6. A Schwartzite nanoporous carbon analogue, boron-doped, which binds hydrogen at 0.14 eV/molecule in density functional theory. Blue is carbon, red, boron and green, hydrogen.

the scope of possible carbon-based hydrogen storage materials by examining in first principles calculations a new set of polymer-based materials. This new concept in hydrogen storage designs into the substrate large static electric dipole moments, so that the hydrogen/substrate interaction is not simply the van der Waals interaction of correlated fluctuating dipoles, but an enhanced interaction of a static dipole (of the substrate) with an induced dipole (of the H_2). Preliminary calculations suggest that this mechanism does increase the H_2 physical adsorption binding energy significantly. Other novel geometrically constrained geometries, also with open-shell configurations or large local fields, are also being investigated, with encouraging preliminary results.

Conclusions and Future Directions

Our synthesis approaches to produce high surface area materials with high boron content are progressing 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. We plan to further increase the boron content (>10 wt%), porosity ($>2,500$ m^2/g), and hydrogen binding in these nanoporous boro-carbons, with computational guidance on optimizing surface chemistry via induction of high curvature, electron deficiency, large local fields, and exposed orbitals that are resistant to aggregation. We will disperse low Z metals in our materials that we have demonstrated computationally are atomically stabilized via interaction with B. These efforts are focused on obtaining very large densities of homogeneously distributed binding sites of 15-30 KJ/mol binding energy in a lightweight framework, which will enable attainment of DOE 2010 targets for gravimetric and volumetric storage and provide a pathway to 2015 goals. Work to date has led to 100% improvement in binding energy (halfway to

the goal) and recent work on optimizing surface area in the heavily boron-doped systems has led to a 200% improvement (comparable further improvements are needed). The effect of increased binding energy of high surface area nanoporous boro-carbons on processes such as hydrogen spillover from noble metals like Pt will also be examined in detail.

FY 2007 Publications/Presentations

1. R.K. Mariwala and H.C. Foley, *Ind.Eng.Chem.Res.*, **33** (1994) 2314.
2. "X-ray Diffraction and H-Storage in Ultra-Small Palladium Particles", Kishore, D.G. Narehood, H.Goto, J.H. Adair, J.A. Nelson, H. R. Gutiérrez, P.E. Sokol, and P.C. Eklund, *Adv. Materials* (submitted).
3. "Transparent Boron-doped Nanotube Films", X.M. Liu, H.E. Romero, K.Adu and P.C. Eklund, *NanoLetters* (submitted).
4. "Transparent Boron-doped Nanotube Films", X.M. Liu, H. Gutierrez and P.C. Eklund. March Meeting of the American Physical Society, Mar 5-9, 2006 (Denver).
5. "Hydrogen Storage in Boron-doped SWNTs", P.C. Eklund, Meeting on Hydrogen Generation, Storage and Fuel Cell Cars, November 14, 2006 (Penn State University).
6. "Gas Nanotube Interactions", P.C. Eklund, June 18–25, NT'06 (Nagano, Japan).
7. M. Chung, V. H. Crespi, P. Eklund, and H. Foley, Advanced Boron and Metal Loaded High Porosity Carbons, The 2007 DOE Hydrogen Program Review Meeting, May 15-18, 2007, Arlington, VA (oral presentation).
8. Physisorption of Hydrogen on Boron-Containing Carbon (B/C) Material Prepared by Organoborane Precursor, Z. C. Zhang, W. Chen, and T. C. Mike Chung, *ECS Transactions*, 2007 (in press).