DOE Hydrogen Program

2007 DOE Hydrogen Program

Advanced Boron and Metal Loaded High Porosity Carbons

Mike Chung, Vince Crespi, Peter Eklund and Hank Foley

Pennsylvania State University

May, 2007

Project ID: **ST # 8**

Overview

Timeline

- Project start: 2/1/05
- Project end: 1/31/10
- % complete: 40%

Budget

- Total project funding
  - DOE share: $1.2M
  - Contractor share: $0.3M
- FY06 $ 225,000
- FY07 $ 333,000

Partners

- Dispersed throughout HSCoE: NIST (neutron), NREL (TPD), Air Products (vol. ads.), UNC (NMR)
- M Dresselhaus (MIT)
- Carbolex, Inc

Barriers addressed

A: *System Wt & Vol:* Hydrogen volumetric (1.5 kWh/L) and gravimetric (6wt%) storage density goals for 2010

B: *System Cost:* High-volume low-cost synthesis routes (via pyrolysis, arc)

C: *Energy Efficiency:* Low pressure, moderate temperature operation (via enhanced binding energy through chemical modification)

E: *Charge/discharge rate:* via Mixed micro/mesopore structures through precursor design

J: *Thermal management:* via designed moderate binding energies of mixed physi/chemi-sorption

P: *Improved understanding:* via calculations in close coupling with fundamental measurements on well-characterized, well-ordered systems

Objectives/Approaches

Achieving DOE 2010 H_2 storage goal (6 wt%) by developing advanced H_2 adsorption materials with high binding energy (10-30 kJ/mol) and high SSA (> 2000 m^2/g)

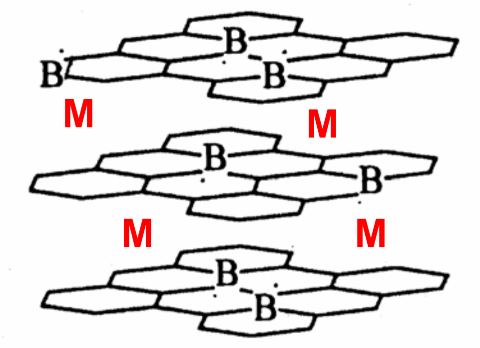
FY06

- Developing methods to prepare porous B/C (B-substitution) materials.
- Characterizing new B/C materials and structure-property-H_2 adsorption relationship.

FY07

- Synthesizing the desirable B/C materials with B content (>10%) and SSA (>2000 m^2/g).
- Investigating routes to prepare atomic metal dispersion (M-intercalation) in B/C materials.
- Studying structure-property relationship.
- Theoretical prediction of M/B/C materials.

M/B/C material



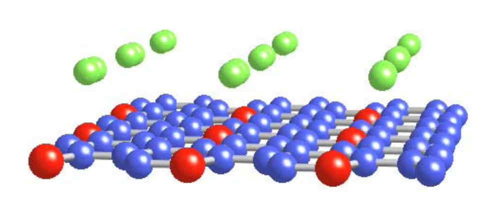
Substitutional B in C

- ✓ *Lightness of Boron*
- ✓ *Enhancing H_2 interaction*
- ✓ *No serious structural distortions*
- ✓ *Catalyzing carbonization*
- ✓ *Stabilizing atomic metal*

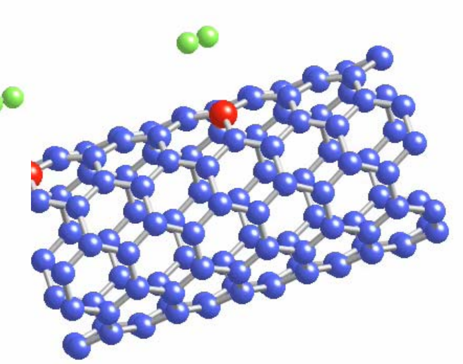
Theoretical Prediction of M/B/C Materials

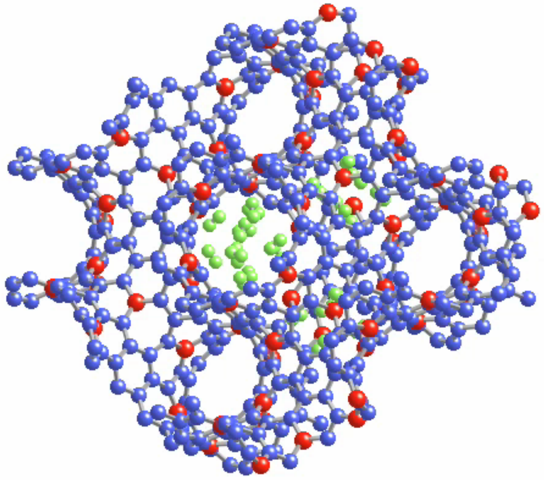
B/C Material (H B C)

7 kJ/mol/H_2



11 kJ/mol/H_2



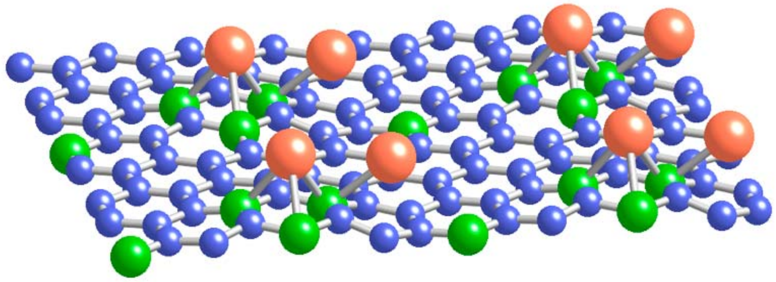


14 kJ/mol/H_2

Boron substitutions of the carbon framework have shown the raise of binding energy to H_2 into the range of theoretical prediction.

M/B/C material (Sc B C)

20-30 kJ/mol/H_2



4.3 eV gained by depositing Sc on B/C surface (ScB_2)

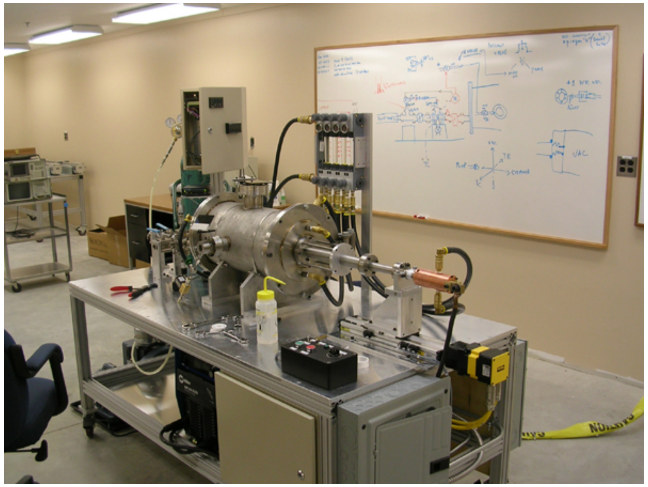
We have predicted that boron doping stabilizes atomically dispersed metals (Sc, Mg, Ti, Pd, Be...) against aggregation, a necessary condition to expose orbitals for reversible hydrogen binding.

(Vince Crespi)

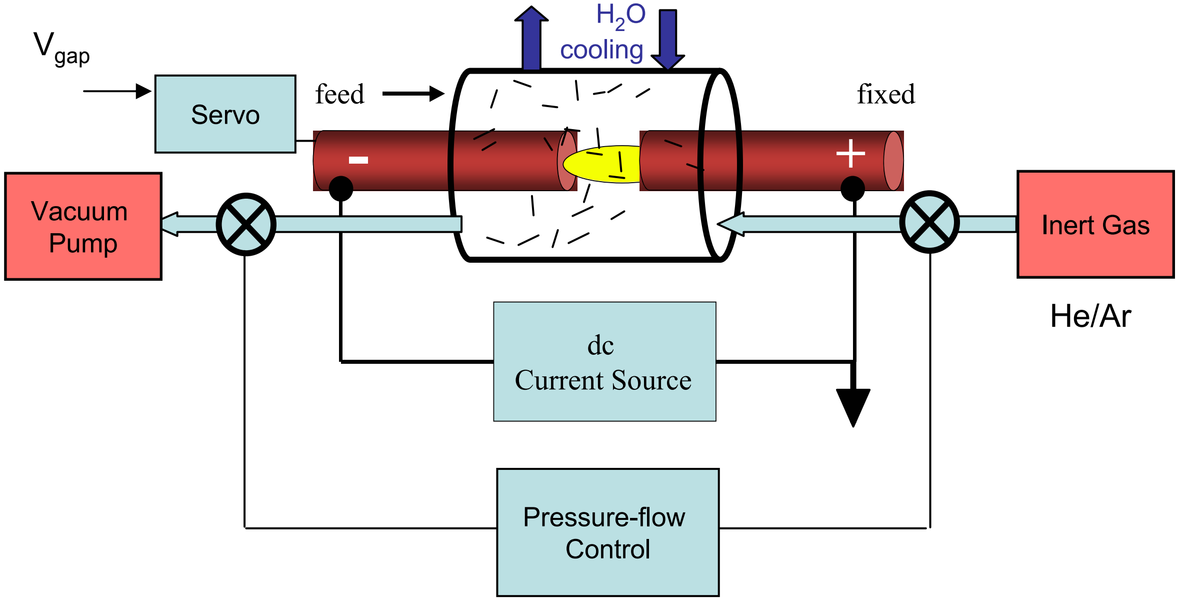
Three complementary approaches to prepare B-substituted carbon (B/C) materials

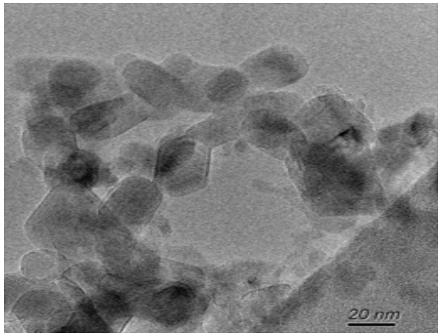
- Electric arc vaporization from M-B-C Electrodes *(Eklund)*
  - *Non-equilibrium high-energy conditions*
  - ***Accomplishment:*** *Production of highly ordered uniform high SSA B-doped carbon nanotubes with boron doping up to 3%, which shows enhancement of* H_2 *binding energy by inelastic neutron scattering. Production of Al-B-nanocarbon particles (~20 nm dia) from Al-B-C electrodes.*
- Molecular Reaction / Pyrolysis *(Foley)*
  - *Combinations of precursors to control complex pyrolitic decomposition*
  - ***Accomplishment:*** *Synthesis of highly porous materials with a controlled mixture of micropores (for large storage) and mesopores (for rapid transport)*
- B-Containing Precursores (Polymers) / Pyrolysis *(Chung)*
  - *Ability to design precursors with high B contents and high SSA*
  - ***Accomplishment:*** *8% boron incorporation into* sp^2 *carbon frameworks. Data show the* increase of H_2 binding energy (~10 KJ/mol) and doubles H_2 absorption capacity.

Synthesis of Nanoparticle Carbides by Electric arc vaporization



Hot-pressed
Metal-Boron-Carbon electrodes
(auto feed if necessary)





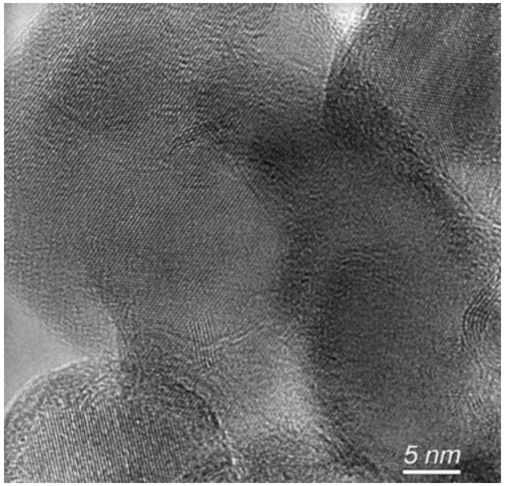
$Al_8B_4C_7$, Al_4C_3 particles
(d~10-20 nm)

- ***Crystalline metal-boro-carbides produced.***
- ***Research Reactor capacity ~100 g/hr (scalable).***

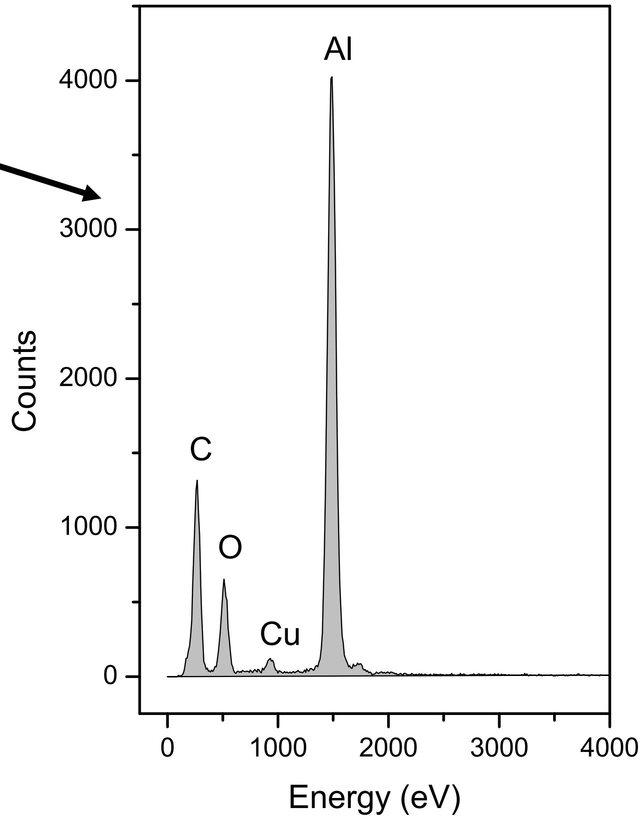
(Peter Eklund)

Al-B-C Nanoparticles (20-100 nm diameter)

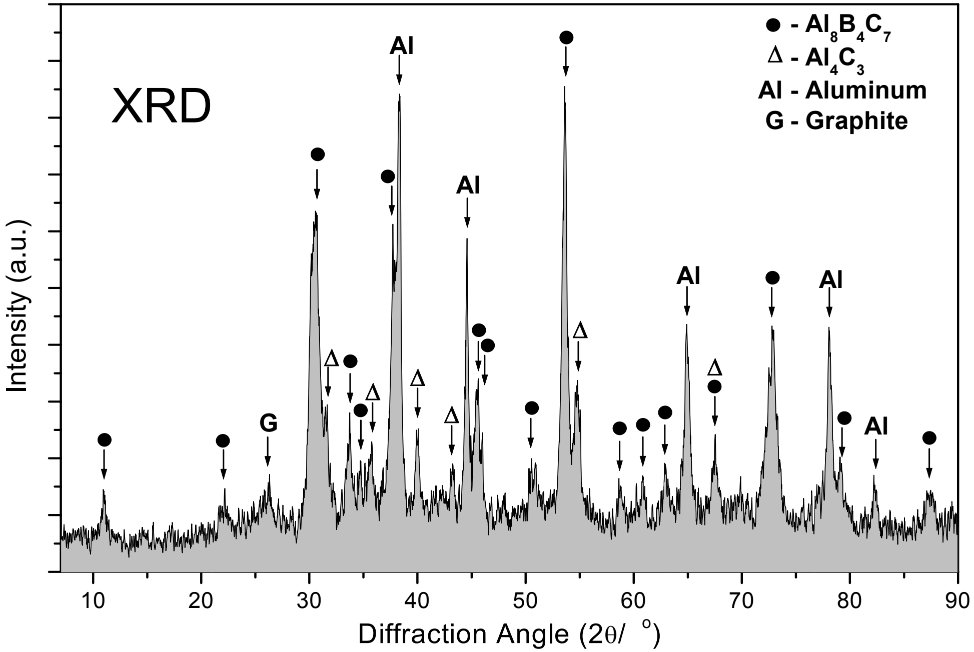
HRTEM



TEM-EDS



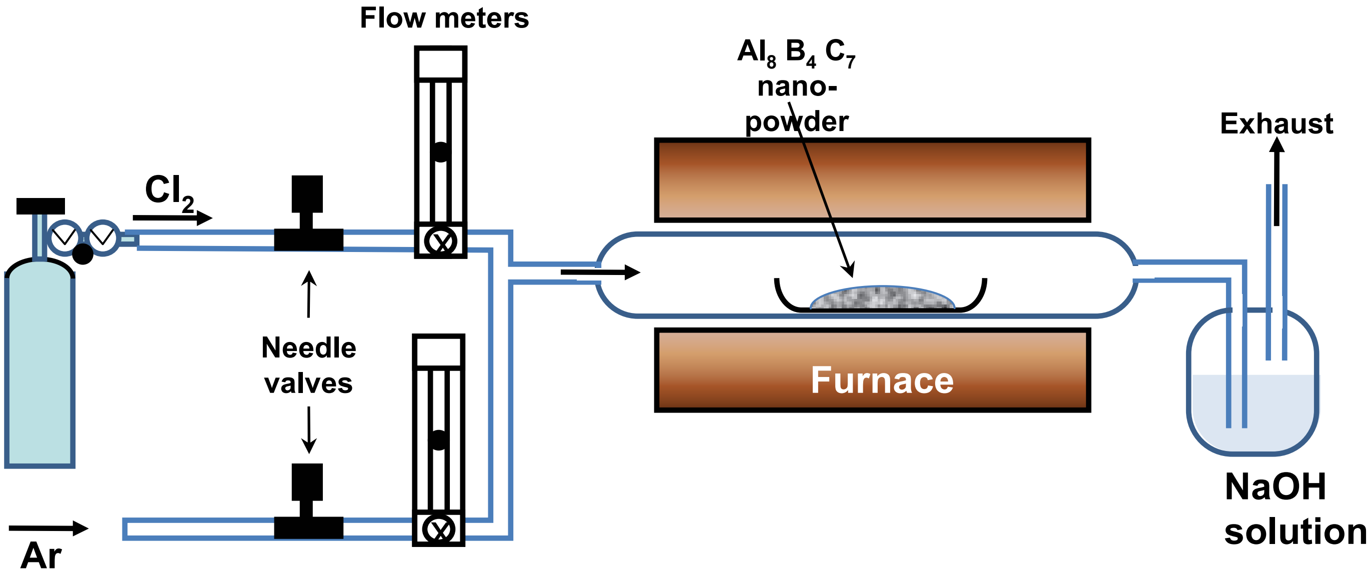
XRD



(Peter Eklund)

Crystalline Al-B-Carbides are produced by Electric arc vaporization

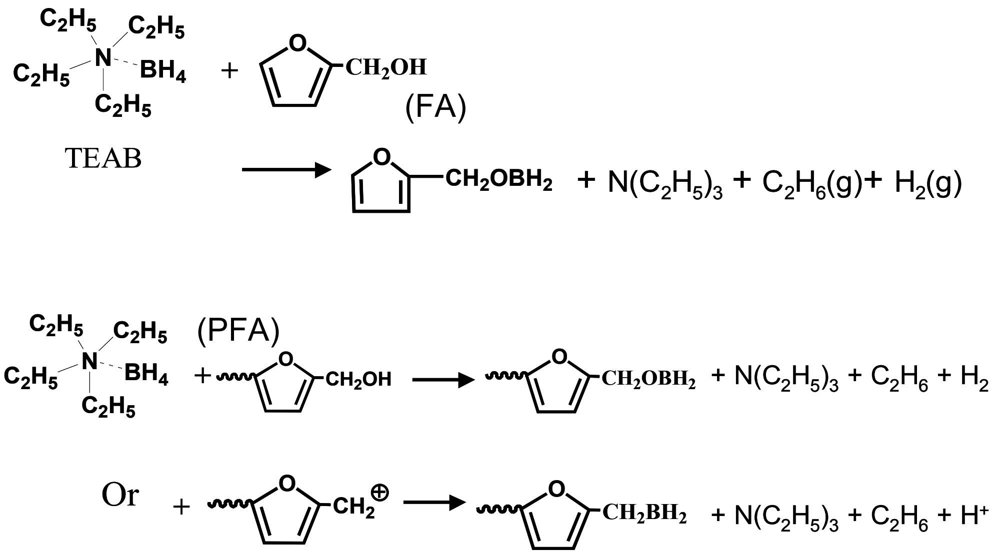
Metal Atom Removal by Cl_2

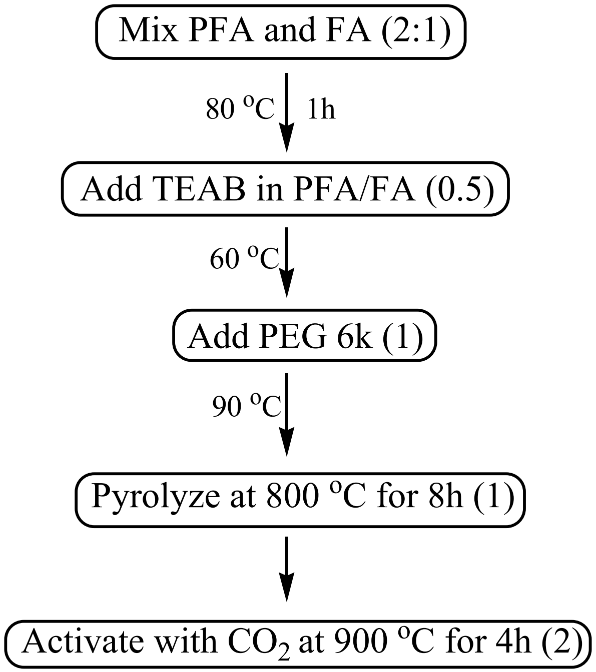


- It is known that Cl_2 will vapor transport not only the metal atoms, but also boron from bulk carbides
- We are exploring non-equilibrium conditions that lead to preferential metal removal leading to a porous boro-carbon with residual metal sites—the residual metal should also be active for H_2 chemisorption
- Encouraging experiments are in progress

(Peter Eklund)

Synthesis of B/C Materials by Molecular Reaction/Pyrolysis





Mix PFA and FA (2:1)

80 °C 1h

Add TEAB in PFA/FA (0.5)

60 °C

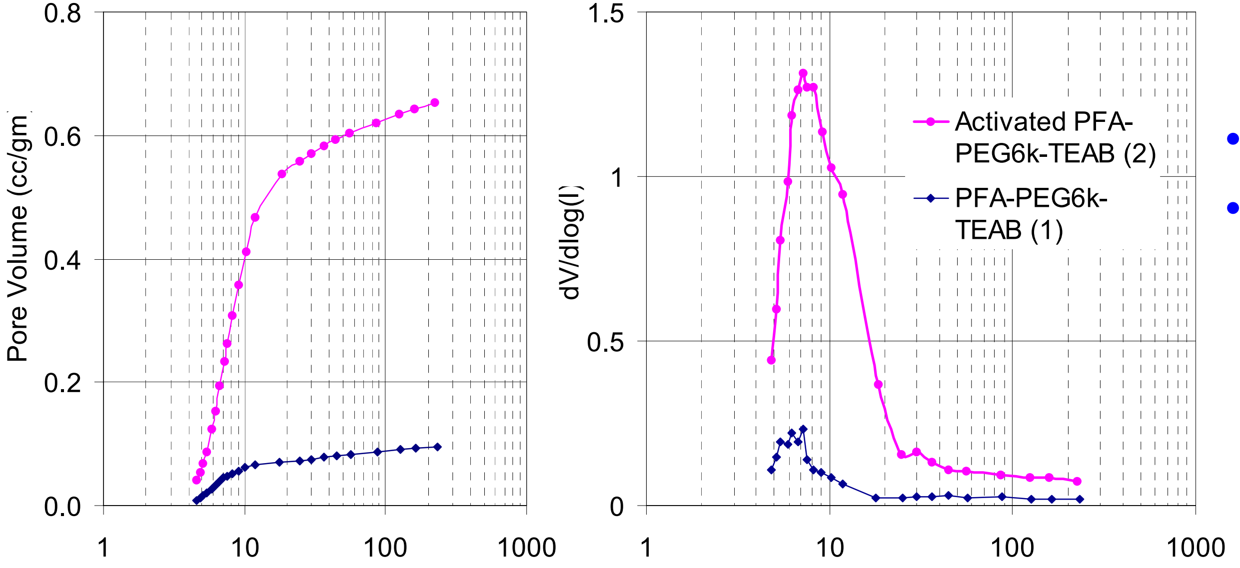
Add PEG 6k (1)

90 °C

Pyrolyze at 800 °C for 8h (1)

Activate with CO_2 at 900 °C for 4h (2)

Pore Size Distribution



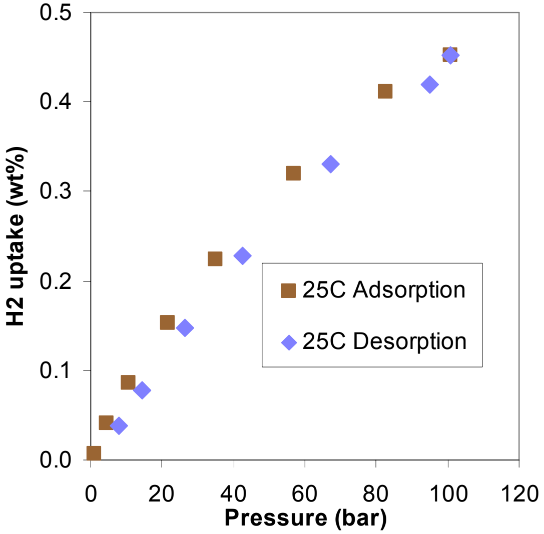
- BET surface area =980m^2/g.
- B:C (atomic%) for sample before activation was 1:60 and after activation was 1:20 respectively

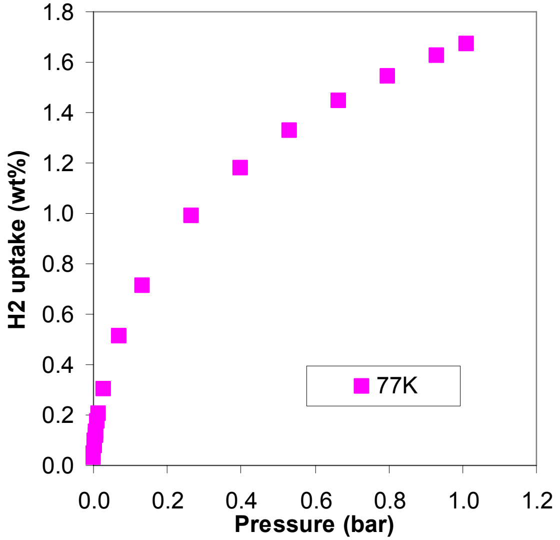
(Hank Foley)

Hydrogen storage measurements

Measurement at NREL	TEAB-1	TEAB-2
N2 BET SSA, as received	35 m^2/g	~950 m^2/g
Sieverts RT H2 Uptake at ~2 bar, as received	<0.01 wt%	0.025 wt%
Sieverts 77 K H2 Uptake at ~ 2 bar, as received	0.2 wt%	1.5 wt%
Sieverts 77 K H2 Uptake at ~ 2 bar, after 200ºC vacuum degas		2.0 wt%
N2 BET SSA, after 200ºC vacuum degas		1071 m^2/g

TEAB-1 and TEAB-2 are the B/C materials before and after CO_2 activation at 900°C for 3 hs.

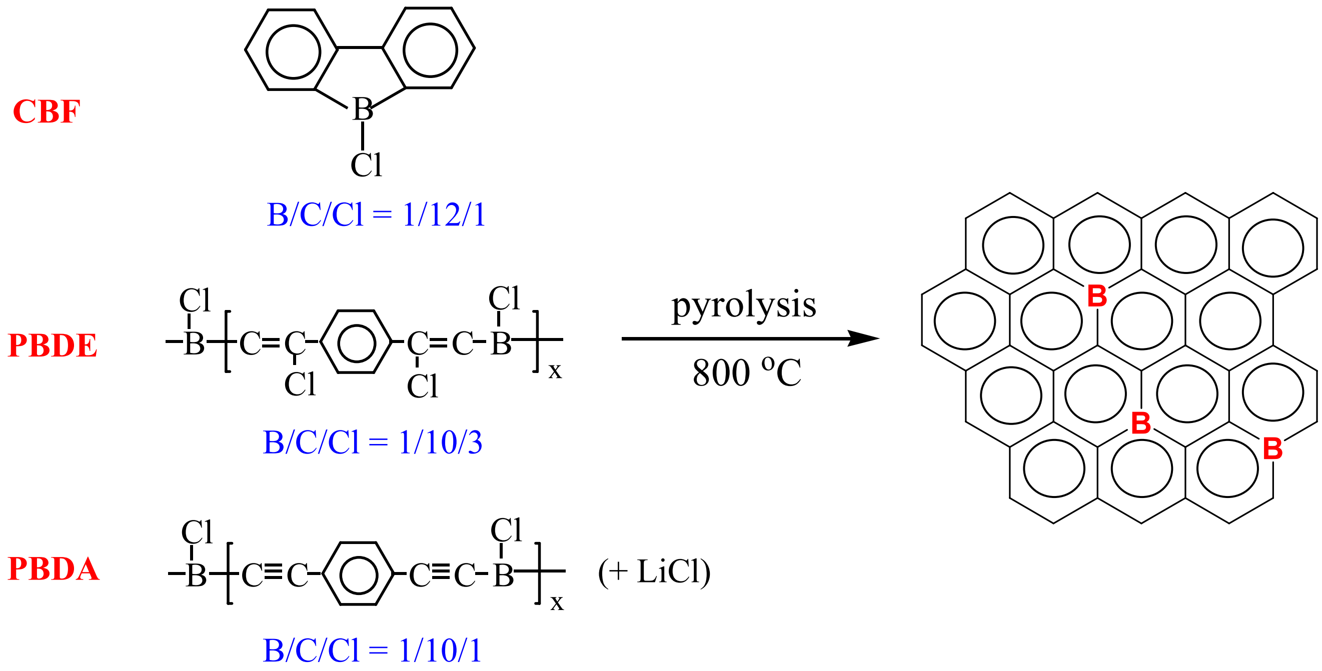




At room temperature, high pressure hydrogen uptake values (0.5 wt% at 100 bar) are similar to activated carbon that has twice the surface area of TEAB-2

(Hank Foley)

Synthesis of B/C Materials by Using B-containing Precursors



(I) from CBF

Dense B/C
8 % B content

(II) from PBDE

150 m^2/g
1.5 % B content

(III) from PBDA

528 m^2/g
5.7% B content

(IV) from PBDA
(at 600 °C)

780 m^2/g
6.5% B content

Precursor Design

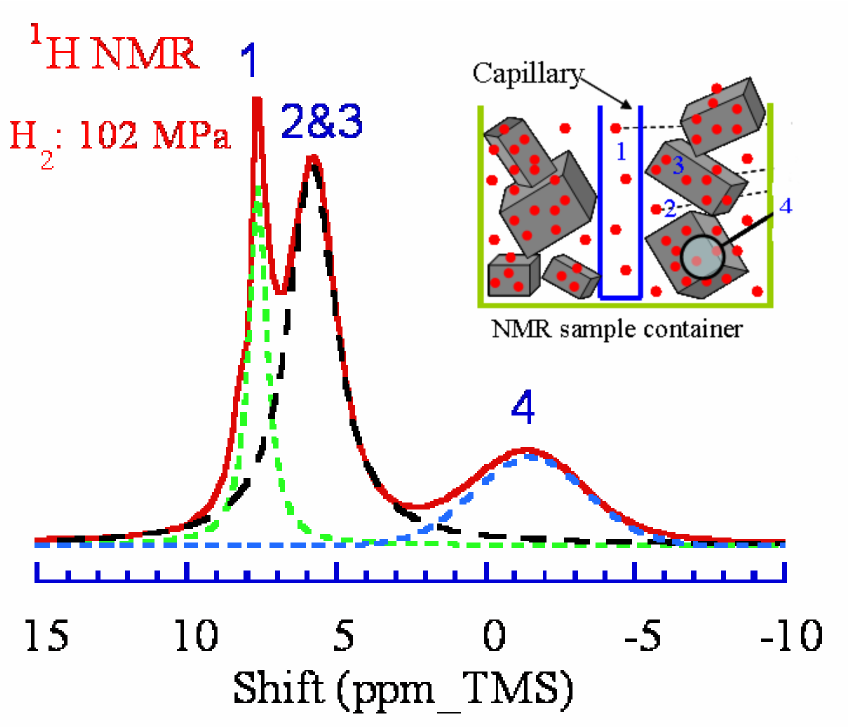
- **Aromatic (conjugated) framework**
- **Strong B-C Bond and Reactive B-Cl bonds for inter-molecular and intra-cyclization reactions**

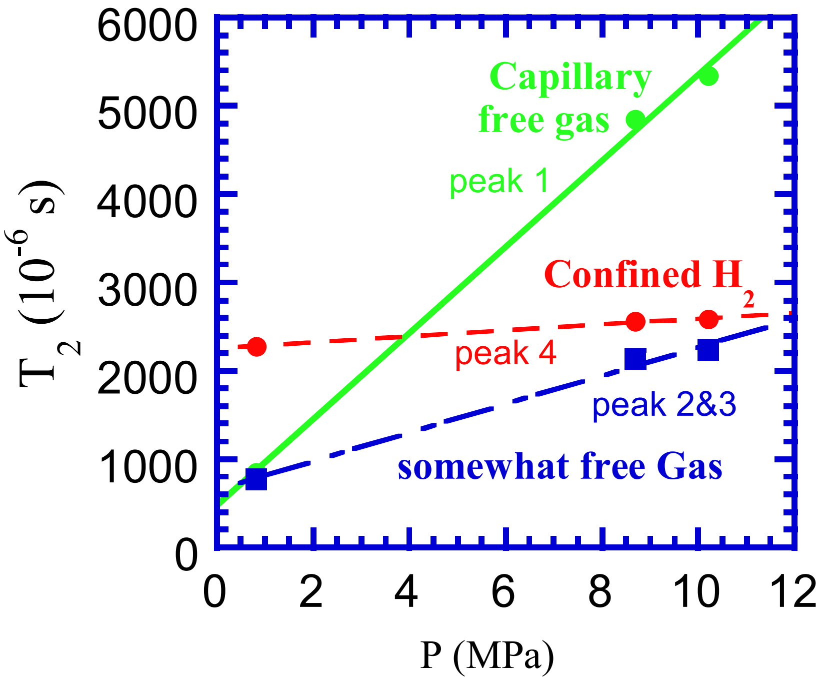
Economic process for producing large scale material, with the control of B content, crystal structure, morphology (SSA, pore size and distribution)

(Mike Chung)

^{1}H NMR spectrum of H_2 Gas in the presence of B/C Material (II)

(1.5 % B content and 150 m^2/g SSA)





Peak 1 and peak 2&3 depend linearly on pressure as expected for free H_2 gas
Peak 4 shows nonlinear pressure dependence. Using the Langmuir equation, an estimate of binding energy ***E_{ads}* =9.2 kJ/mol** (> 3 times higher than C).

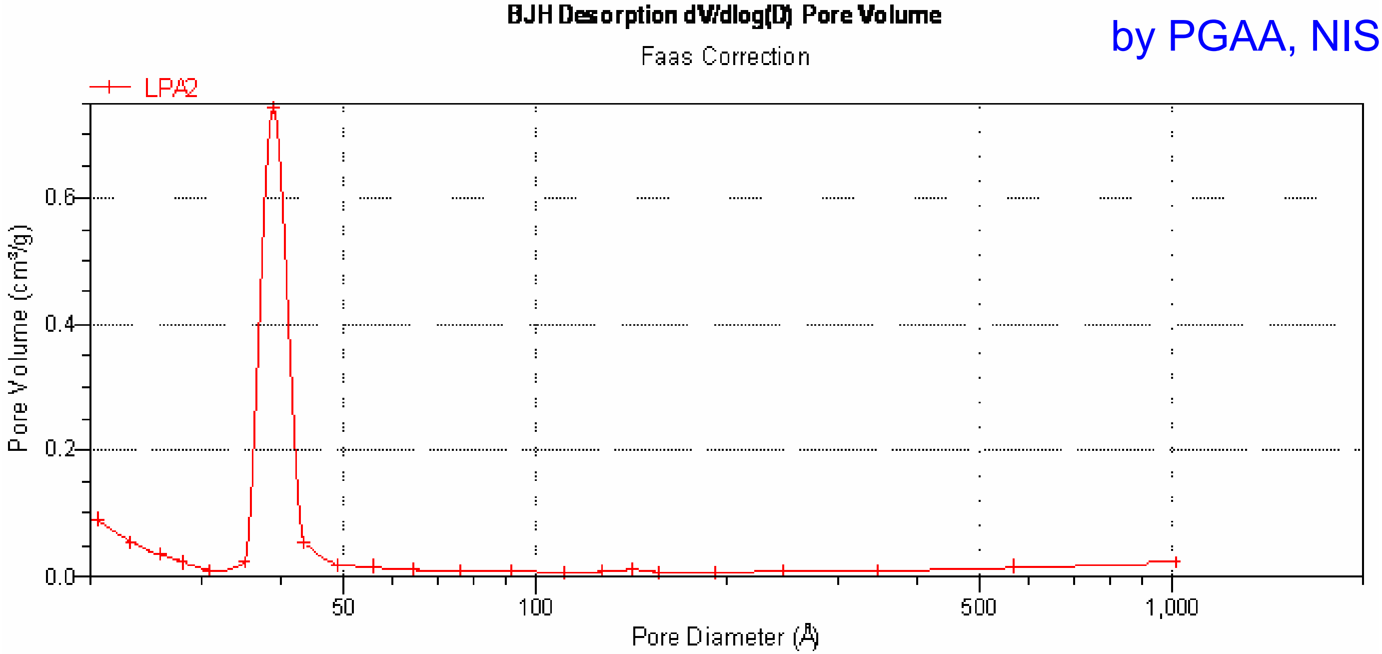
Boron significantly enhances H_2 binding energy

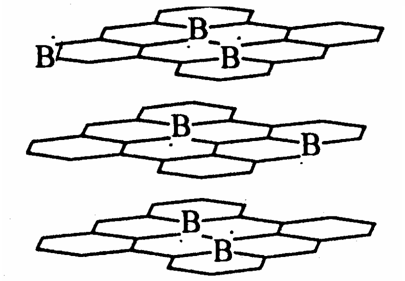
Yue Wu (UNC) and Mike Chung

Pore Size Distribution in B/C Material (III)

(B content = 5.7%; Surface area= 528 m^2/g)

B content measured by PGAA, NIST





+ NR_3 tridodecyl amine →

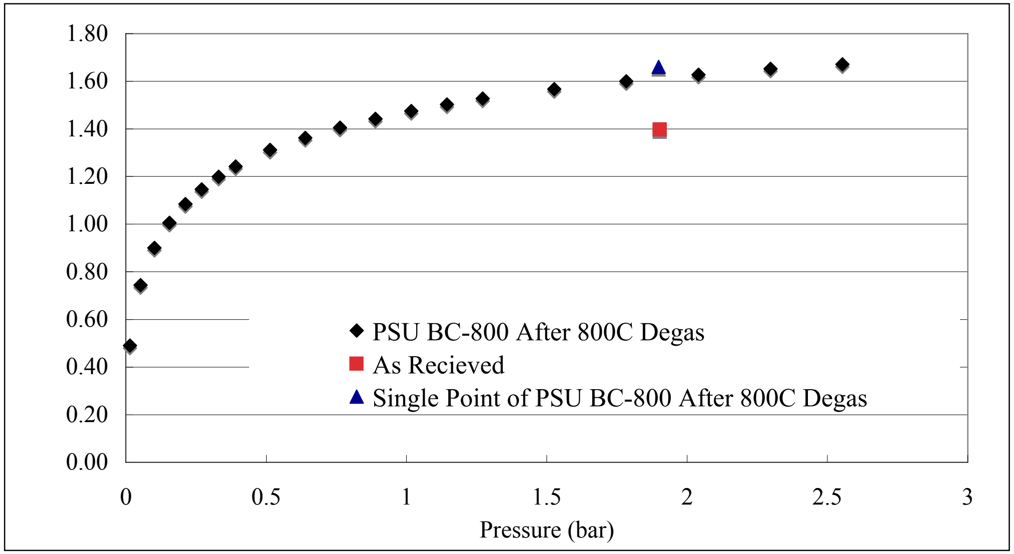
Double the weight of B/C material
37% of B atoms form B-N complexes

About 1/3 of the incorporated B atoms are available for interaction

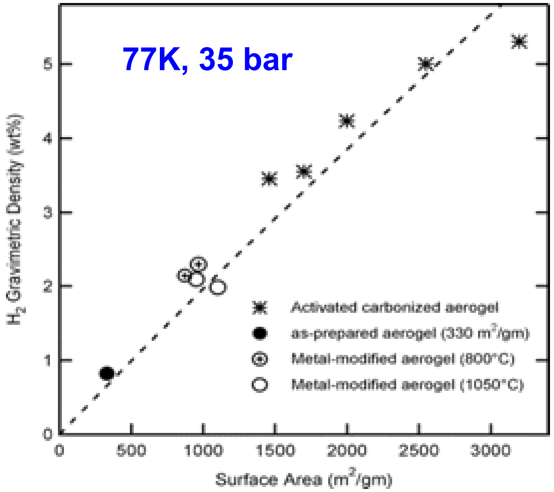
(Mike Chung)

Hydrogen Uptake in B/C Material (III) (NREL)

Measurement		**PBDA (BC-800)**	**PBDA (BC-1500)**
N_2 BET SSA, as received		**528 m^2/g**	**33 m^2/g**
Sieverts RT H_2 Uptake at ~2 bar, as received		**0.02 wt%**	**0.004 wt%**
Sieverts 77 K H_2 Uptake at ~ 2 bar, as received		**1.4 wt%**	**0.07 wt%**
TPD from 77 K to 800ºC		**Physisorption only**	**Physisorption only**
BET after 800ºC degas		**619 m^2/g**	
Sieverts 77 K H_2 Uptake at ~ 2 bar, After 800ºC degas		**1.6 wt%**	



C Materials



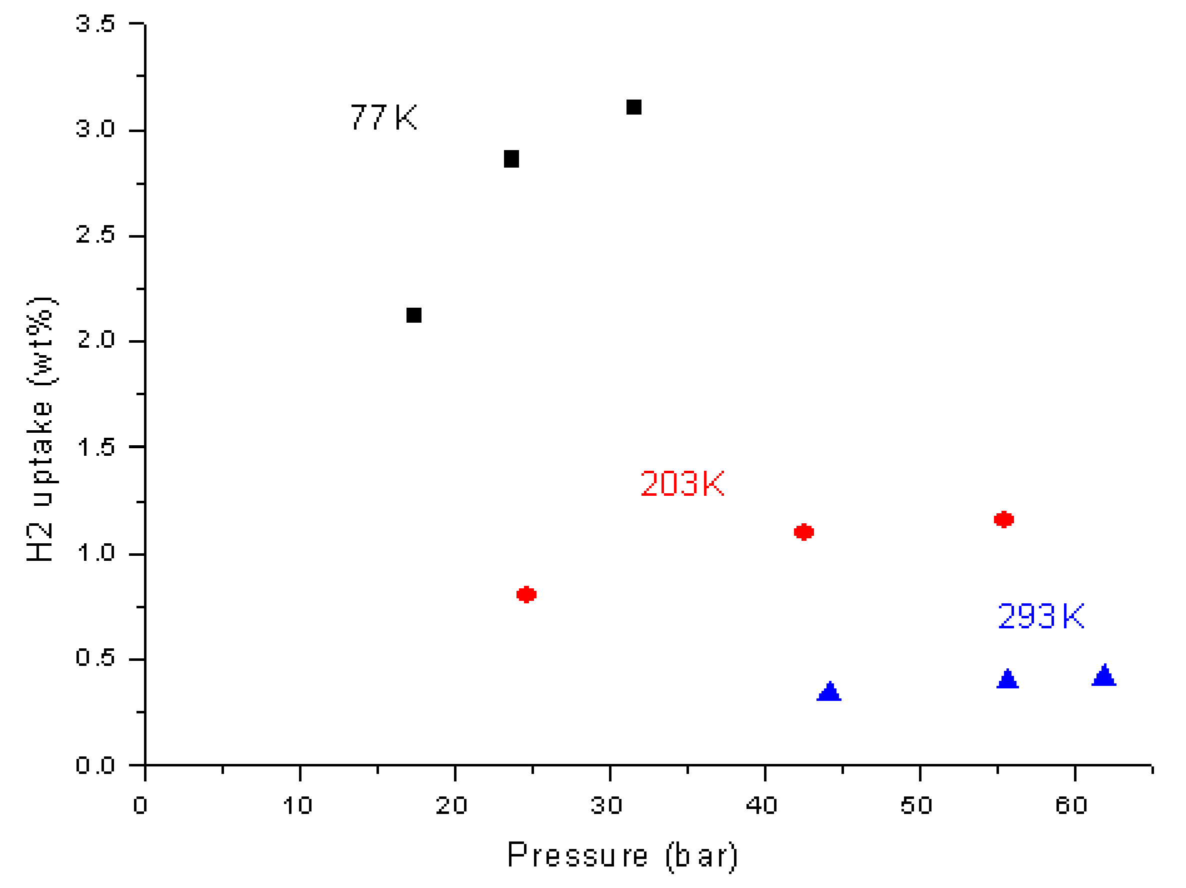
Ahn et al, Chem. Mat. 18, 6085, 2006

B/C material (vs. C with a similar SSA) shows >50% increase in H_2 uptake at 2 bar

(Mike Chung)

Hydrogen Uptake in new B/C Material (IV)

(B content = 6.5%; Surface area= 780 m^2/g)



- The corresponding C material with a similar surface area only adsorbs < 2% H_2 at 77K and 30 bar.
- Reversible Adsorption-Desorption cycles by pressure

B/C material (vs. C with a similar SSA) doubles H_2 adsorption at 77K

(Mike Chung)

Summary: Penn State Effort

- **Relevance:** Increase reversible hydrogen BE by developing new storage materials through chemical modification of carbon frameworks.
- **Approach:** Three complementary synthesis techniques closely coupled to adsorbtion measurements and first-principles materials theory.
- **Technical accomplishments:**
  - All three synthesis routes produce boron-substituted sp^2 carbon (B/C) materials.
  - B/C materials have been prepared with up to 8% substitutional B elements and SSA ~1000 m^2/g.
  - B/C material increases H_2 binding energy (~10 kJ/mol) and doubles absorption capacity.
  - Calculations show that higher boron content in higher-curvature geometries have higher binding energy (~30 kJ/mol) and boron stabilizes atomically dispersed metals on the carbon framework.
- **Collaborations: NREL, NIST, UNC, AirProducts, Carbolex**

Future Work

Plan for the rest of FY07

- Continuing the development of new B/C materials with more reactive B species, B content (>10%) and surface area (>2000 m^2/g), which further increase storage capacity at high temperatures.
- Studying the correlation between B species (structure, morphology) and H_2 Binding Energy.
- Investigating synthesis protocols for metal dispersion onto B/C materials to further increase binding energy and raise the operating temperature.

Plan for FY08

- Pushing B content to >20% and surface area > 2000 m^2/g in various forms of B/C materials to further increase binding energy and determine (T,P) needed for 6 wt% reversible H_2 storage.
- Developing the desirable Metal-Boro-Carbon materials (specific metal, composition, and morphology) and investigate bi-functional (B & metal) H-storage.

Summary Table

Comparison of Hydrogen Storage in Various Material Systems

Material	**Binding Energy** (KJ/mol)	**H_2 Adsorption**		
		Wt (%)	**Temperature** (K)	**Pressure** (atm)
C material (1000 m^2/g SSA)	**~ 3**	**0.3 2**	**300 77**	**50 30**
B/C material (IV) (6.5% B content; 780 m^2/g SSA)	**> 10**	**0.5 3.2**	**300 77**	**50 30**
M-B-C Material (calculation)	**30-80**	**> 5**	**300**	**1-10**

Our intent is to optimize the material to meet the 2010 goals with higher boron concentrations, greater surface areas, and metal dispersion for bi-functional (physical/chemical) adsorption & storage.