Advanced Boron and Metal Loaded High Porosity Carbons

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The Pennsylvania State University

Project ID#: STP 11

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Overview

Timeline

- Project start: 2/1/05
- Project end: 1/31/10
- % complete: 60%

Budget

- Total funding for PSU team
  - 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)

Barriers

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

Project Objectives and Approaches

6 wt% H_2 storage goal by increasing binding energy (10-30 kJ/mol) and SSA (> 2000 m^2/g)

Micro-porous

B Substitution C

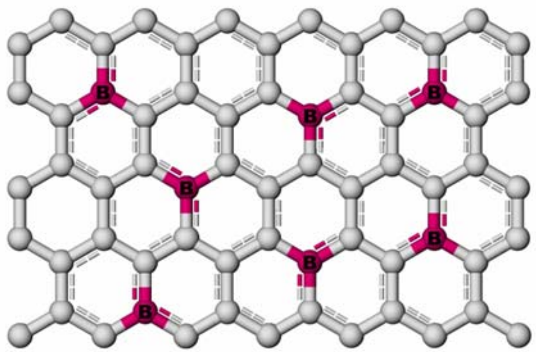
(B/C) Materials

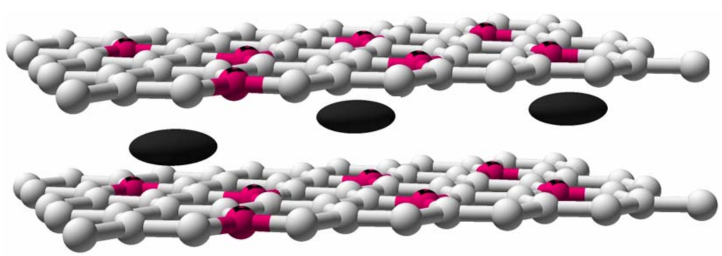
↓

Microporous

Metal Intercalation

M/B/C Materials





B in C Structures

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

Project Activities and Schedule

FY06

- Developing synthesis routes and processes to prepare 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 high B content and high SSA, and their H_2 adsorption.
- Investigating synthesis routes to prepare atomic metal dispersion (M-intercalation) in B/C materials.

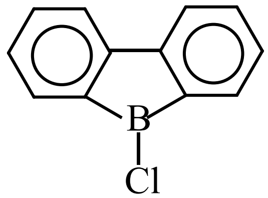
FY08

- Synthesizing the desirable B/C and M/B/C materials with B content (>10 mol%), M content (>3 mol%), and SSA (>2000 m^2/g).
- Studying structure-property relationship.

Technical Accomplishments

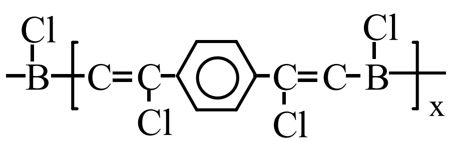
Synthesis of B/C Materials by B-containing Precursors

CBF



B/C/Cl = 1/12/1

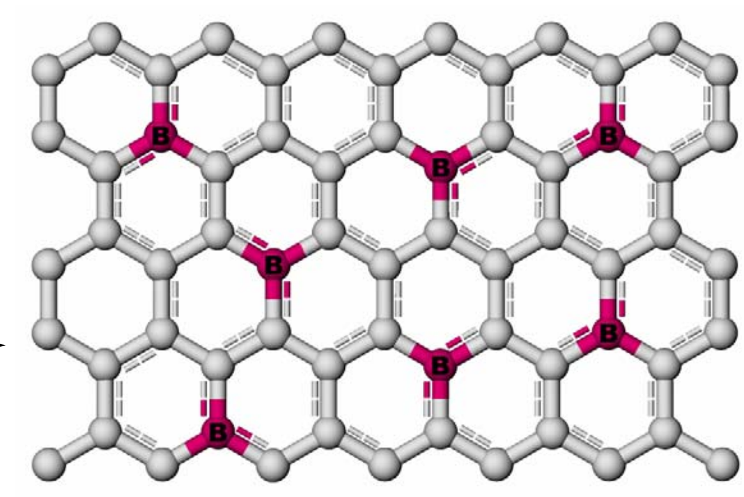
PBDE



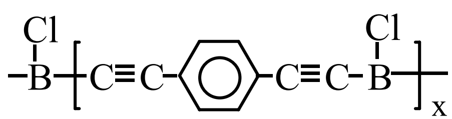
B/C/Cl = 1/10/3

pyrolysis

> 800 ^{o}C



PBDA



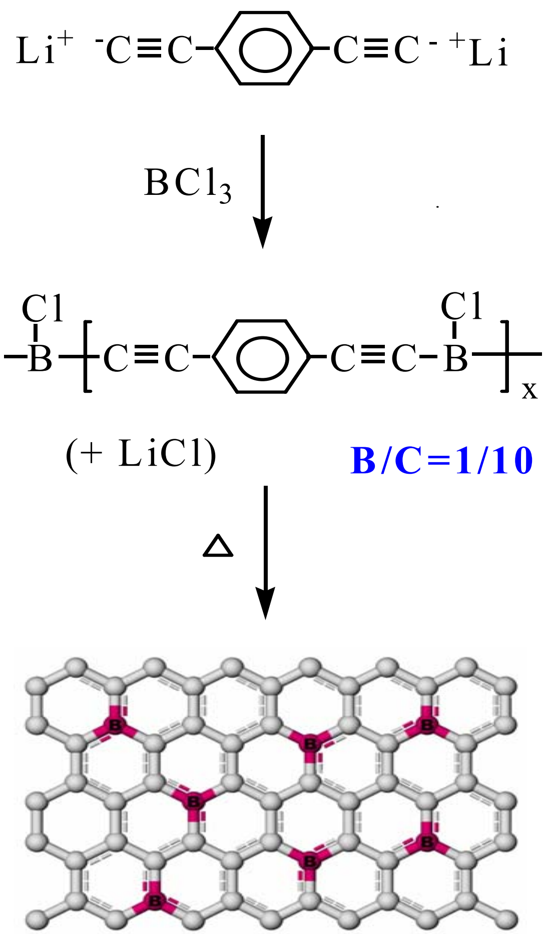
B/C/Cl = 1/10/1

- **Conjugated B-C bonds**
- **Reactive B-Cl for stabilization**

- **Simple process**
- **Large scale production**
- **Varying pyrolysis temp.**
- **Control Crystal structure**
- **Control B content (up to 10%)**

Technical Accomplishments

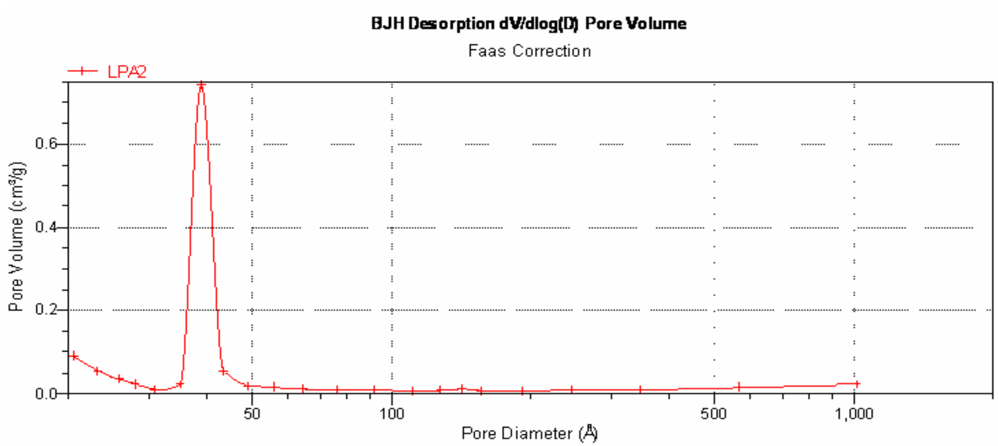
Synthesis of Micro-porous C/B Material



Micro-porous B/C

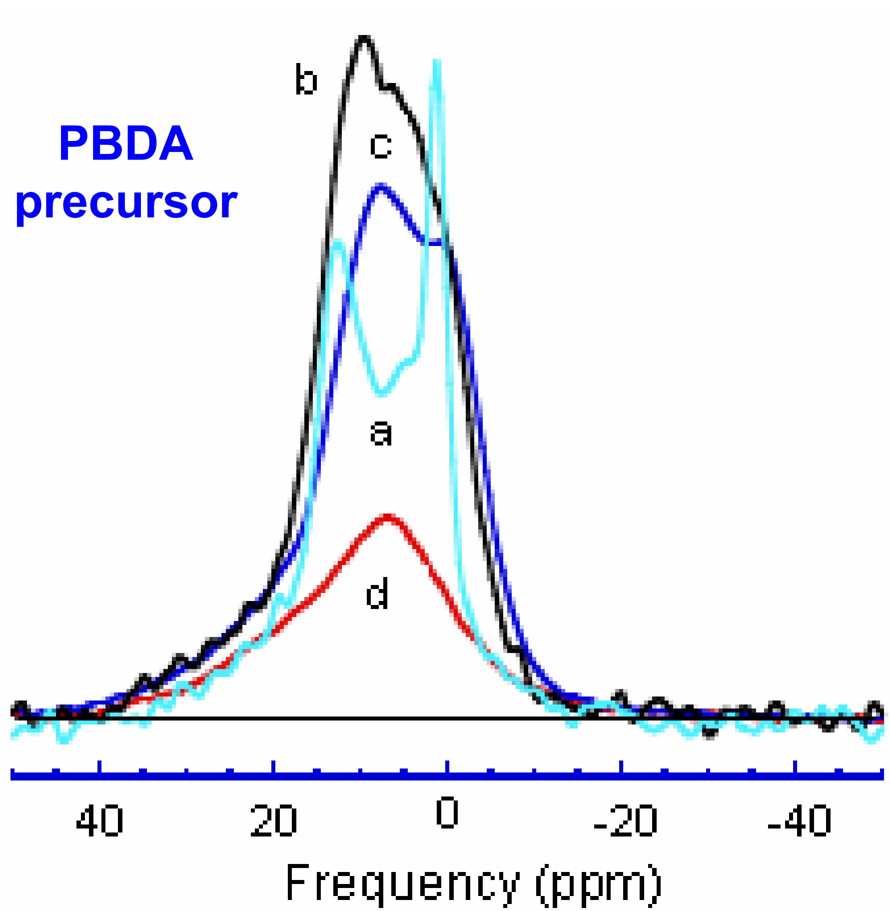
Pyrolysis temp. (°C)	B content[a] (wt%)	B content[b] (wt%)	Surface area[c] (m^2/g)
600	7.2	7.6	780
800	5.7	7.1	528
1500	3.8	3.0	33

a. Prompt Gamma-ray Activation Analysis (NIST).
b. ^{11}B MAS-NMR measurement (UNC).
c. BET method using N_2 gas at liquid N_2.

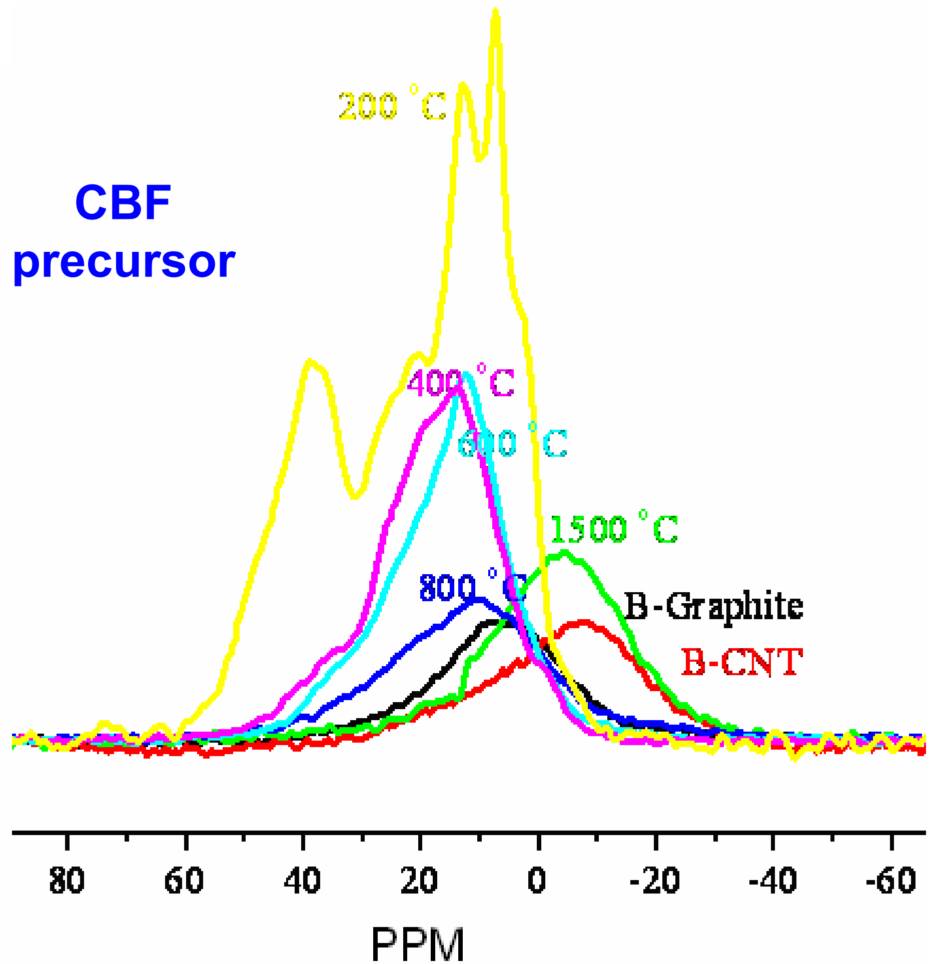


Technical Accomplishments

Solid State 11B MAS-NMR spectra of B/C materials



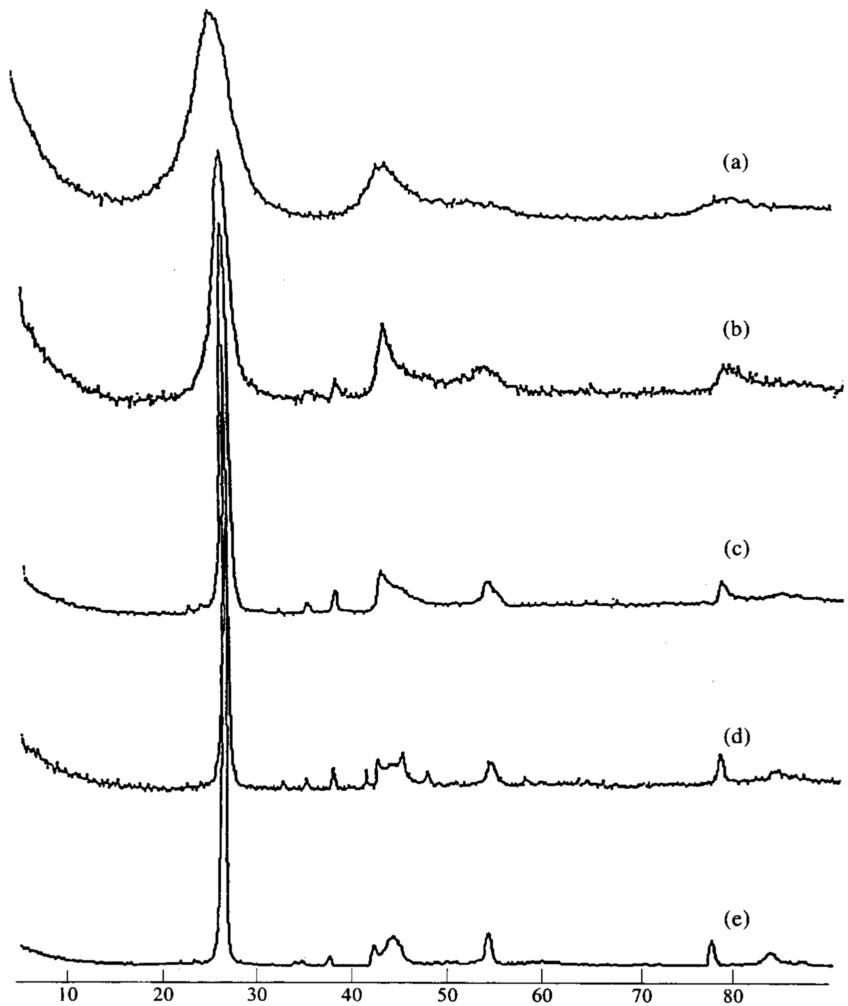
(a) 150, (b) 600, (c) 800, (d) 1000 °C



Yue Wu (UNC) and Mike Chung

Technical Accomplishments

XRD Patterns of C/B materials



Pyrolysis Temp.	D-Spacing (002) (A)	Boron Content
800°C	3.461	7.65%
1500°C	3.411	7.58% (PGAA, NIST)
1800°C	3.383	7.42%
2100°C	3.363	6.96%
2300°C	3.347	3.46%

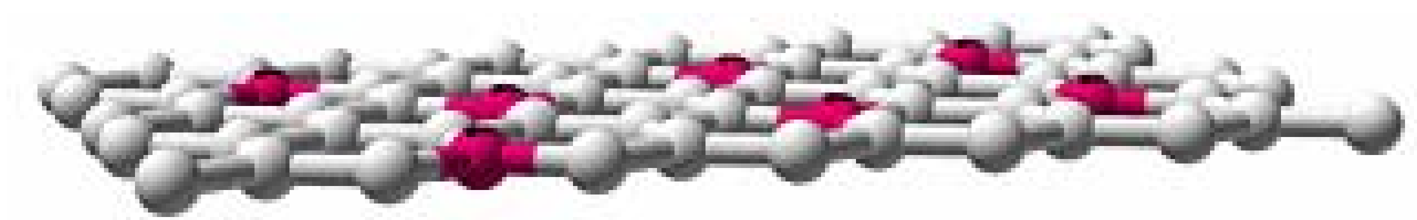
Technical Accomplishments

Evolution of B/C Sructure during Pyrolysis

600 ^oC

1000 ^oC

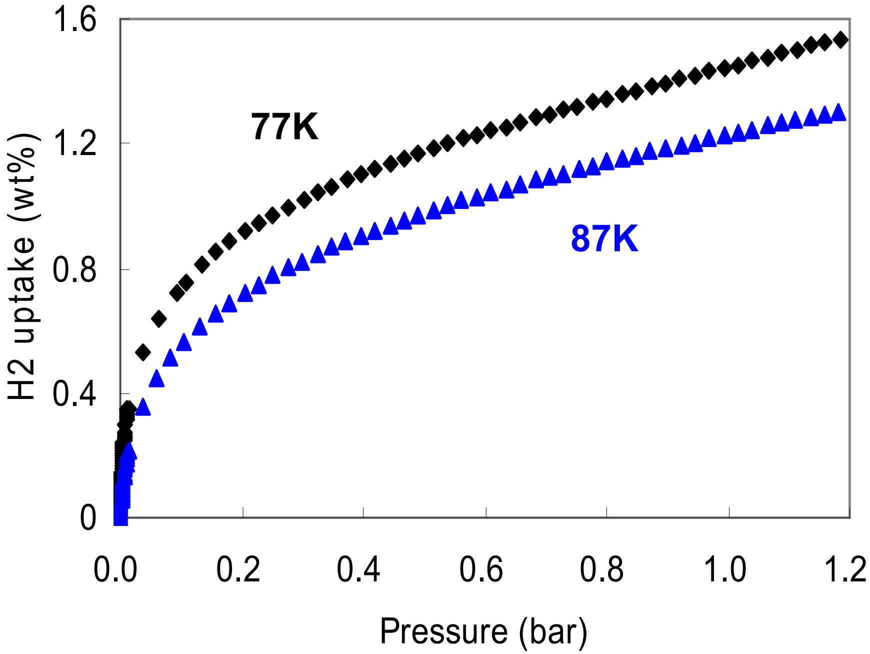
>1500 ^oC

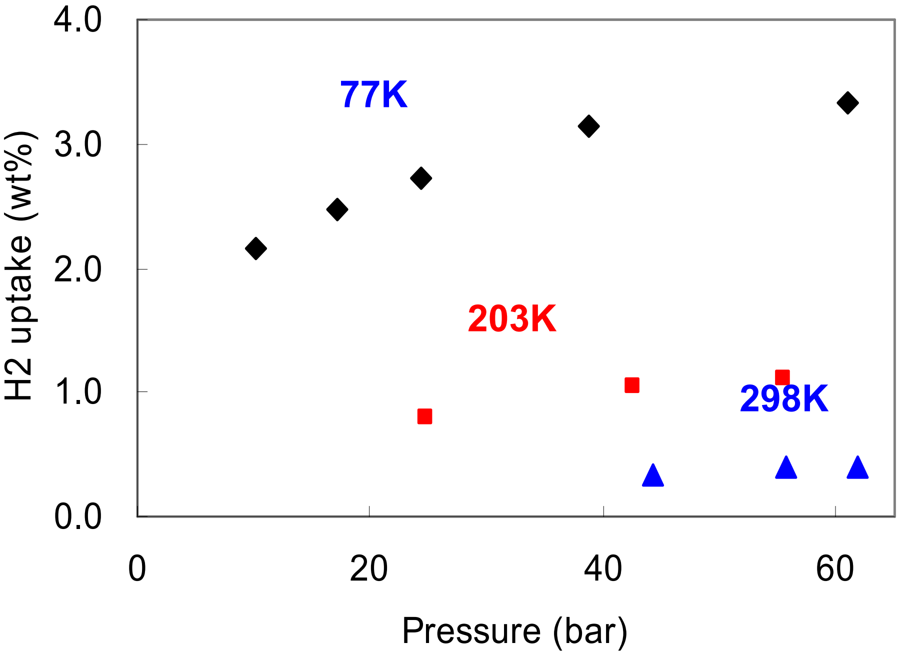


B/C materials with various B site structures that are controlled by pyrolysis temperatures

Technical Accomplishments

Hydrogen Uptake in Micro-porous B/C *(SSA: 780 m²/g)*

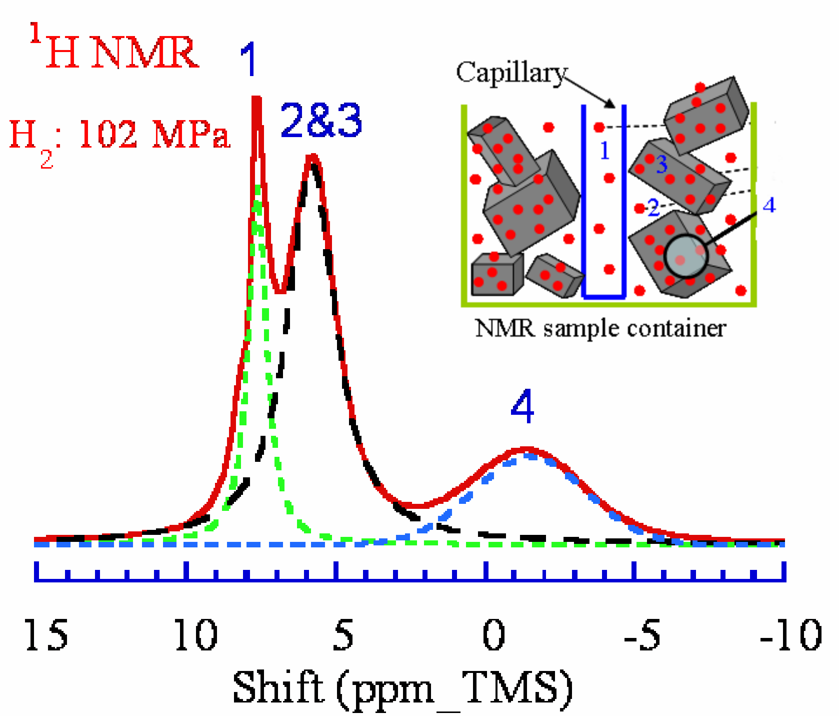


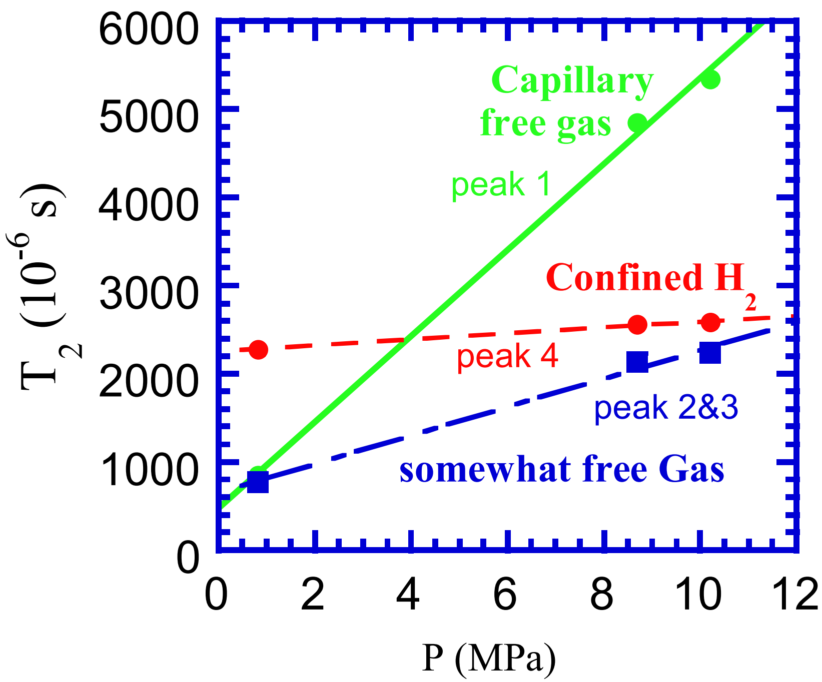


- Initial heat of adsorption for the B/C material is ***12.47 kJ/mol***
- ***About 2 times H_2 adsorption capacity*** (vs. C having similar SSA)

Technical Accomplishments

^1H NMR spectrum of H_2 Gas in Porous B/C Material





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 $\boldsymbol{E_{ads}}$ **=11 kJ/mol**.

Boron significantly enhances H_2 binding energy

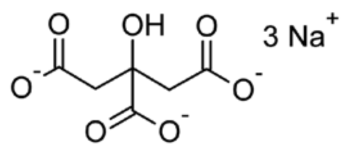
Yue Wu (UNC) and Mike Chung

Technical Accomplishments

Metal-loading in B/C Materials

Graphitic C

H_2PtCl_6



in Water

$NaBH_4$ chemical reduction

Pt(0) particles in C material

B/C material

$Cp^*_2ZrCl_2$ Homogeneous Toluene solution

Washing then Drying

△ 600 °C

Zr/B/C Material

Technical Accomplishments

Comparison of Metal Loading onto C and B/C Materials

Metal Containing Reagents	Activated C (200 mg, 600 m^2/g) After metal loading (mg)	B/C Material (200 mg, 500 m^2/g) After metal loading (mg)
H_2PtCl_6[a]	230	234
Cp_2TiCl_2[b]	200	309
$Cp^*_2ZrCl_2$[b]	205	222
$[(\eta^5\text{-}Cp^*)SiMe_2(\eta^1\text{-}NCMe_3)]TiCl_2$[b]	203	272

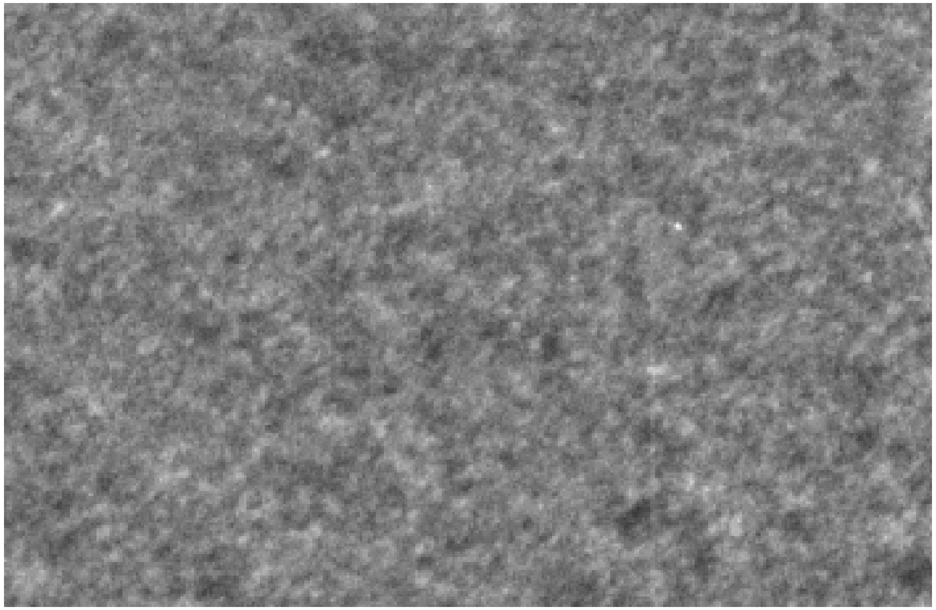
a. Loading in surfactant/water emulsion
b. Loading in toluene solvent (without surfactant)

Substitutional B in C structure enhances metal intercalation

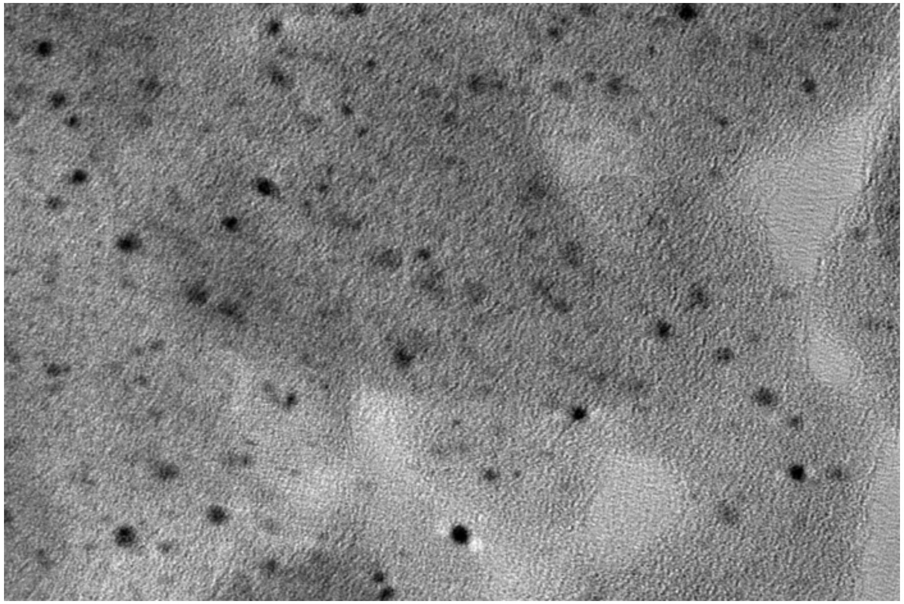
Technical Accomplishments

High resolution TEM Image of Zr/B/C Material

B/C Material with $Cp^{*}_{2}ZrCl_{2}$ $\xrightarrow[600\ ^{o}C]{\Delta}$ Zr/B/C Material



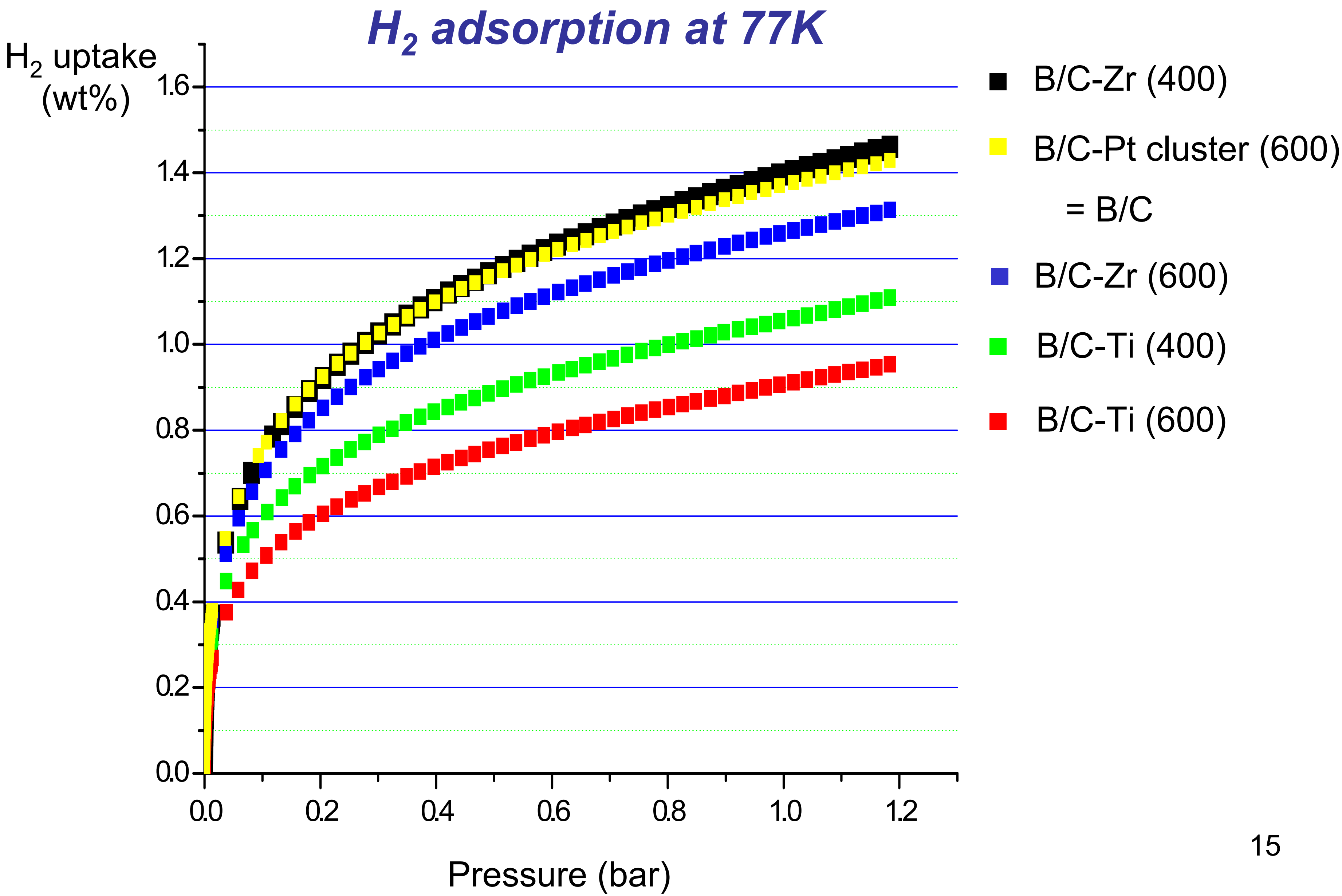
Wave-like B/C structure



Uniform Zr particles (size < 2nm)

Intercalating uniform metal nanoparticles without surfactant

Technical Accomplishments



Summary

- **Micro-porous B/C Materials (B ~8%, SSA ~800 m^2/g)** has been prepared by B-precursor and pyrolysis
- **B/C Structure Changes with Pyrolysis Temp** B moiety gradually immerses in graphitic structure
- **B/C Shows H_2 Binding Energy (~12 KJ/mol) and Double Adsorption Capacity (vs. C)**
- **New M/B/C Materials Have Been Prepared with Intercalated Nano-Metal Particles**

Future Work

Year 08

- Increase Surface Area of B/C Materials

  H_2 adsorption could reach 6 wt% if B/C material would contain > 10% B and >2000 m^2/g

- Increase Binding Energy of M/B/C Materials

  H_2 adsorption at ambient temperature requires higher binding energy (15-30 KJ/mole)

  Finding right M species

  Well-dispersed metal atoms or neat atomic particles

- Spill-over on M/B/C Materials