Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

P. Pfeifer,[1] C. Wexler,[1] P. Yu,[1] M. Lee,[2] D. Robertson,[2,3] L. Firlej,[4] B. Kuchta[5]

[1]Dept. of Physics, [2]Dept. of Chemistry,
[3]University of Missouri Research Reactor (MURR)
University of Missouri, Columbia, MO 65211

[4]Université Montpellier 2, Montpellier, France

[5]Université Aix-Marseille, Marseille, France

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Alliance for Collaborative Research in Alternative Fuel Technology

ALL-CRAFT

Overview

Timeline

- Project start date: 9/1/08
- Project end date: 11/30/14

Budget

- Total Funding Spent*: $1.781M
- Total DOE Project Value: $1.899M
- Total Cost Share: $0.514M

*As of 3/31/14

Barriers

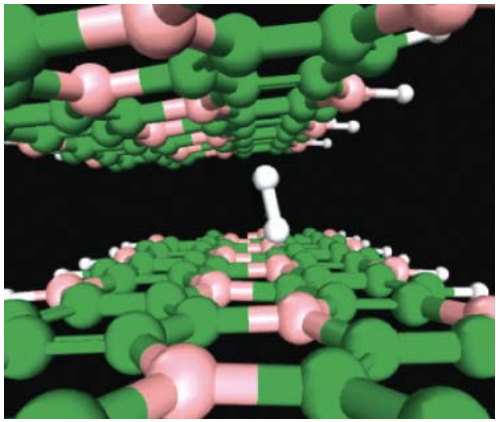
- System weight & volume
- System cost
- Charging/discharging rates
- Thermal management
- Lack of understanding of hydrogen physisorption & chemisorption

Partners

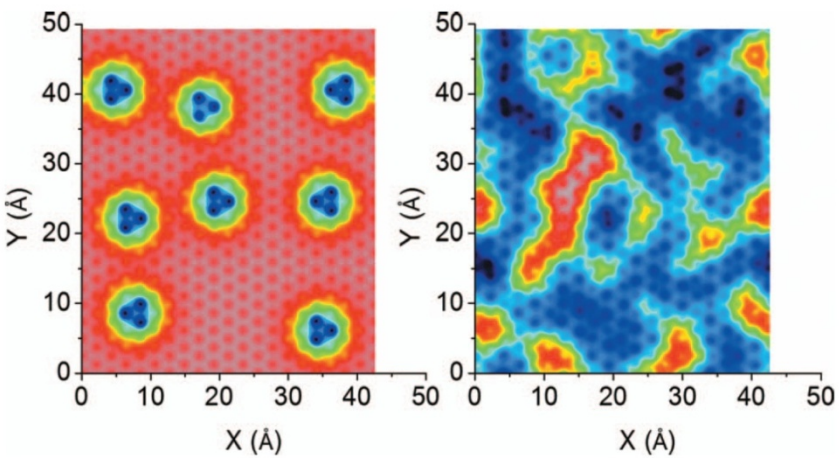
- MeadWestvaco, Charleston, SC
- OsComp, Houston, TX—J. Romanos
- NREL—T. Gennett, P. Parilla
- ORNL—J. Idrobo, R. Olsen
- Missouri U. Science & Technology—D. Waddill
- U. Missouri-Kansas City—P. Rulis
- NIST Center for Neutron Research—R. Paul

Objectives & Relevance

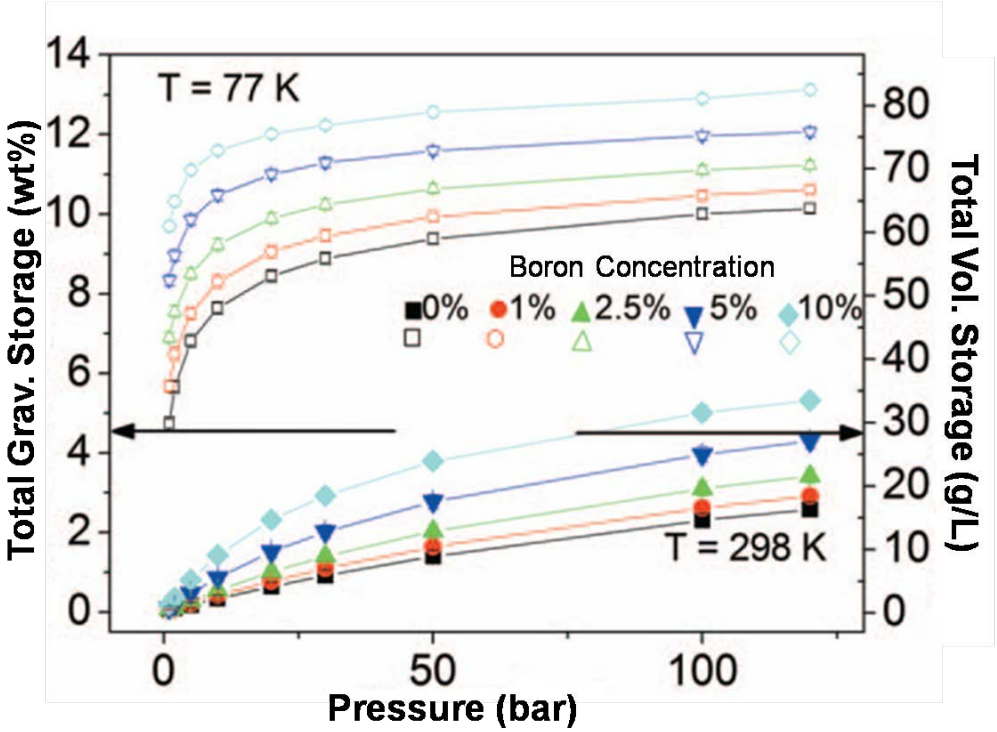
Increase binding energy of H_2 on carbon by functionalization of surface with boron:



- Binding energy of H_2 on graphite: 5 kJ/mol
- Binding energy of H_2 on B-substituted carbon: 10-15 kJ/mol
  Electron donation from H_2 to electron-deficient B
- GCMC simulations of H_2 on 10 wt% boron predict:
  H_2: adsorbent = 5 total wt% at 298 K, 120 bar,
  H_2: adsorbent = 12 total wt% at 77 K, 120 bar

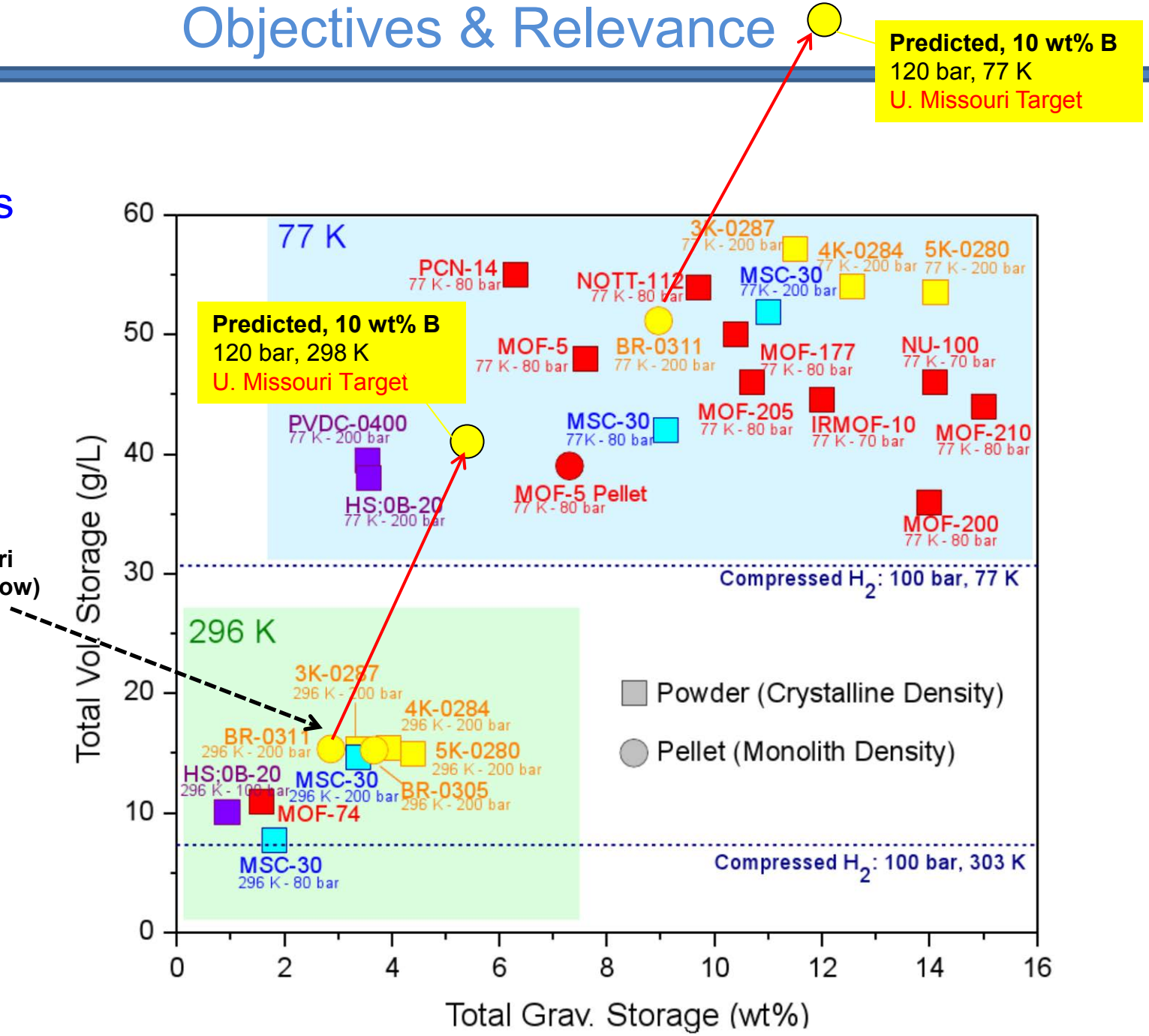


Binding energy landscape: 4.8-9.1 kJ/mol (red-blue) on 1-5 wt% B (left-right)
Firlej et al, 2009; Kuchta et al, 2010



Objectives & Relevance

Objectives relative to existing materials



Approach—Milestones

Objectives	Milestones	Completion
Fabricate boron-doped nanoporous carbon (particulate and monoliths) for high-capacity reversible hydrogen storage	• First create undoped high-surface-area materials; then dope with boron (gas phase, $B_{10}H_{14}$) for high binding energy for H_2	80%
	• Create high-surface-area carbon with minimum pore space, for high volumetric storage capacity	100%, 10/2013
	• Dope materials with <10 wt% B:(B+C) [Redirection Jan. 2014], for high binding energy for hydrogen	80%
	• Establish B-doped materials with surface areas ~2700 m^2/g, binding energies 10-15 kJ/mol, volumetric storage capacity >40 g/L (material), and gravimetric storage capacity >5.5 wt% (material) at 200 bar and room temperature	60%
Characterize materials &demonstrate storage performance	• Establish reproducibility of B-doped materials	100%, 12/2013
	• Establish effective deoxygenation of materials prior to doping	100%, 01/2014
	• Establish B deposition in monoliths	100%, 05/2013
	• Establish that boron is completely and uniformly substituted in carbon lattice (sp^2 B-C bonds)	70%
	• Establish enhanced binding energy and H_2 adsorption on B-doped materials at low coverage [Redirection Jan. 2014]	70%
	• Explore other high-binding-energy carbon materials (alternate approach to high binding energy)	N/A
	• Compute binding energies for relevant pore geometries/chemistries	100%, 01/2014

Technical Accomplishments

Best Performing Carbons (2013-14, reproducible)

	Sample	Surface area (m^2/g)	Porosity	Max. grav. exc. (wt% material)	Total grav. storage (wt% material)	Total vol. storage (g/L material)	Isosteric heat (kJ / mol) at low/high coverage*
Nanoporous Graphene-like Carbons	5K-0280 (77 K, 190bar) (296 K, 190bar)	2700	0.84	5.9 0.9	14 4.4	54 15	N/A, 5.8
	4K-0284 (77 K, 190bar) (296 K, 190bar)	2600	0.81	5.6 1.0	13 3.9	54 15	N/A, 4.7
B-Doped Graphene-like Carbons	4K-0246 (B=4%) (77 K, 190bar) (296 K, 190bar)	2400	0.81	5.1 0.9	12 3.8	52 15	7.5, 5.5
	5K-0215 (B=8%) (77 K, 190bar) (296 K, 190bar)	1900	0.79	4.3 0.7	11 3.3	50 14	9.7, 6.2
Synthetic Nanoporous Carbons	HS;0B-20 (77 K, 190bar)	940	0.46	2.5	3.5	40	9.4, 6.6
	PVDC-0400 (77 K, 190bar)	780	0.49	2.0	3.7	28	10.8, 7.8
Monoliths	4K Monolith (297 K, 100bar)	2100		0.9	2.5	9.5	-
	BR-0311 (77 K, 190bar) (296 K, 190bar)	2300	0.74	4.3 0.9	9.0 2.9	51 15	-
Com-mercial carbon	MSC-30 (77 K, 190bar) (296 K, 190bar)	2700	0.80	5.3 0.9	12 3.6	53 15	N/A, 5.0

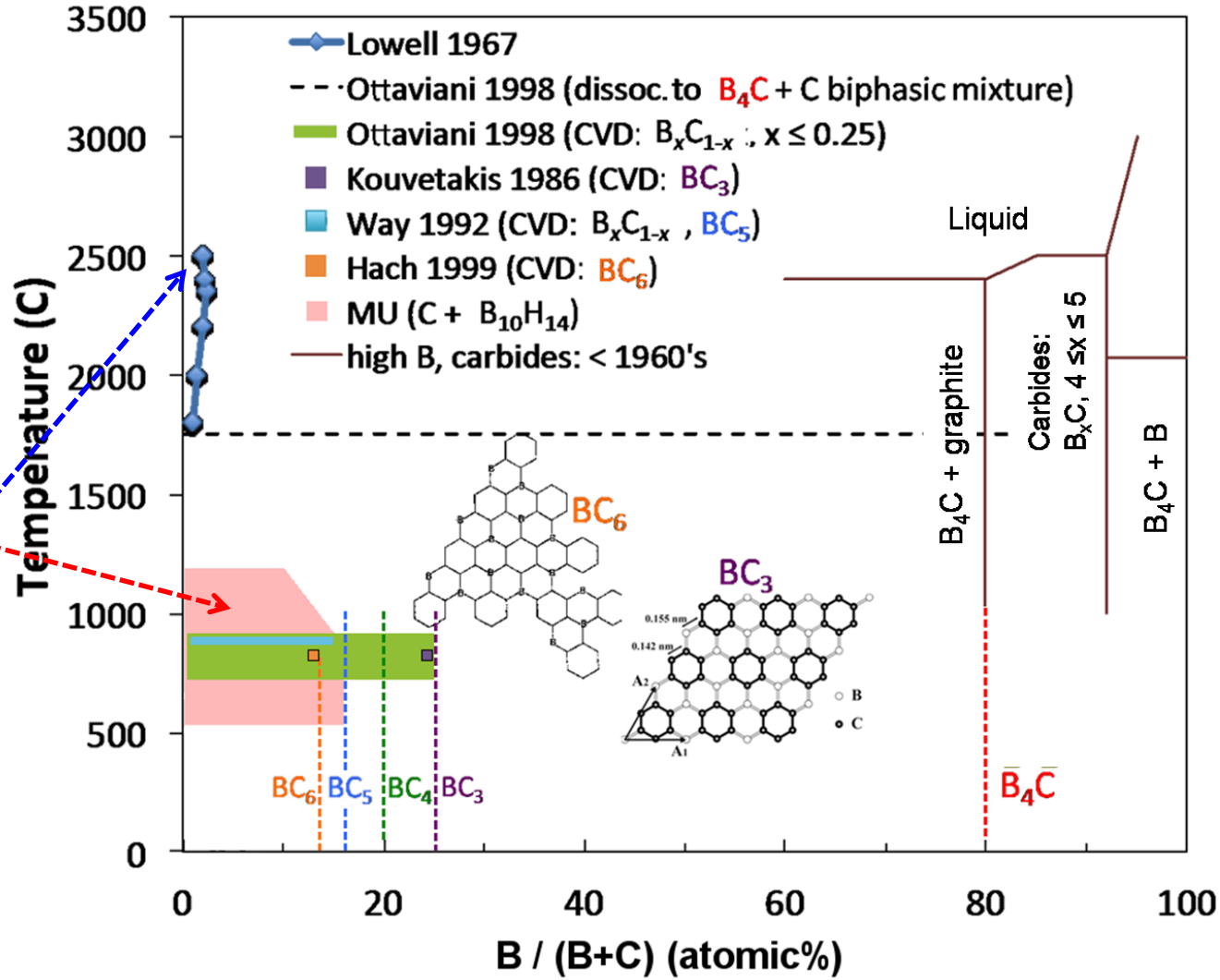
*Low coverage: <0.01 wt% H_2 absolute ads.; high coverage: >1.5 wt% H_2 absolute ads. (2010 AMR)

Accomplishments and Progress

B-C phase diagram

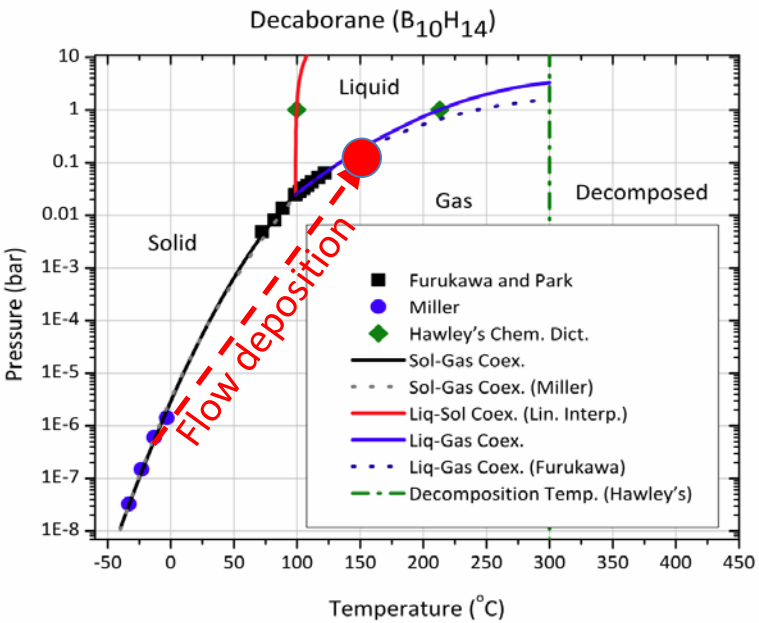
Stable B-C structures as a function of B conc. and temperature:

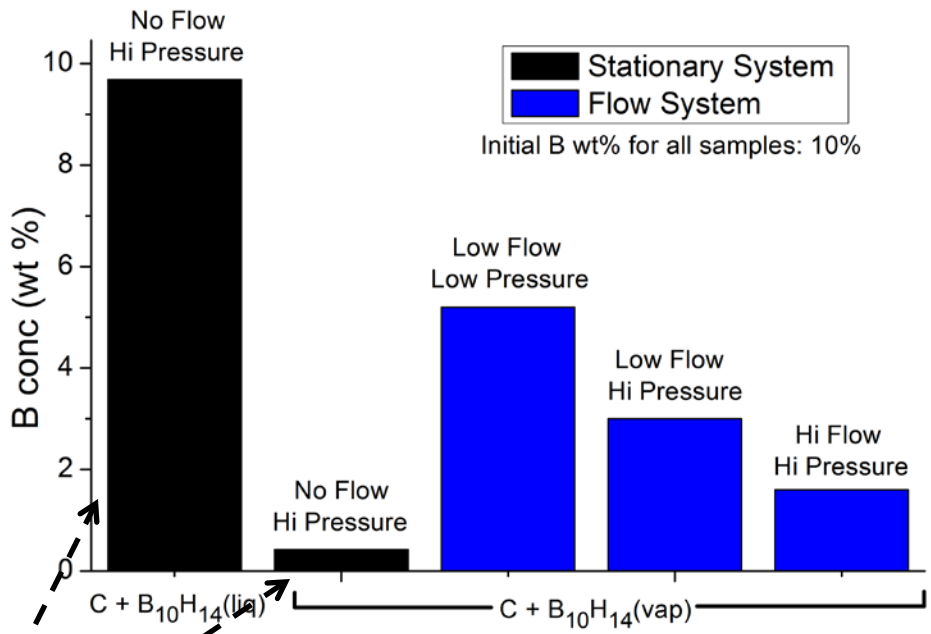
- Single phases or mixtures with variable composition
- Single phases with fixed composition: dashed lines
- U. Missouri-doped materials interpolate between known stoichiometric sp^2-B-C compounds
- "Solubility limit" of 2.3 atomic% is not limit for boron substitution



Accomplishments and Progress

Boron doping I—Deposition & decomposition of $B_{10}H_{14}$



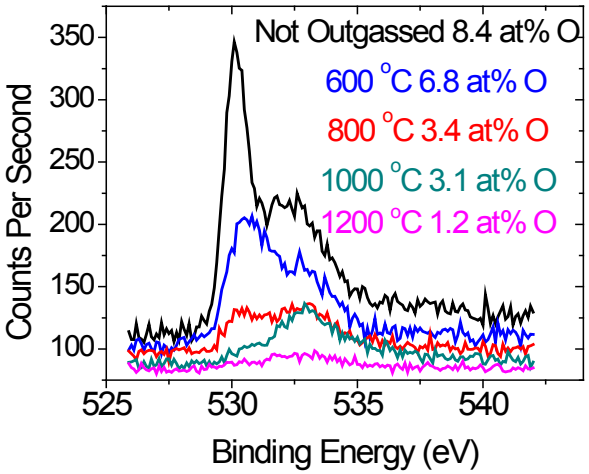


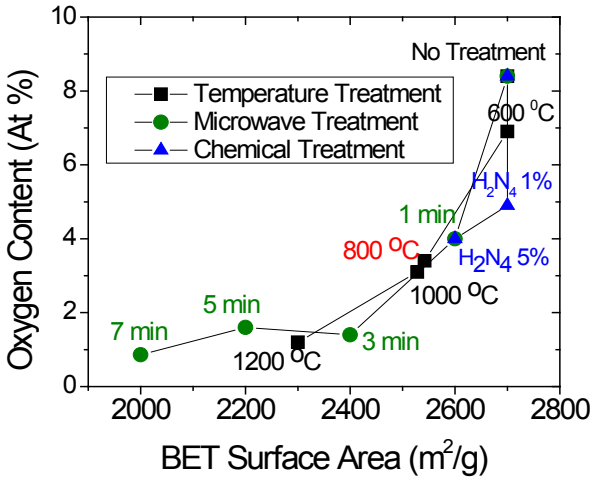
- Stationary (no flow) deposition from liquid $B_{10}H_{14}$: can deposit 10 wt% boron on carbon, but may clog pores.
- Stationary deposition from $B_{10}H_{14}$ vapor: reduces pore clogging, but can deposit only up to 1 wt% boron
- Flow deposition from $B_{10}H_{14}$ vapor (carrier gas: Ar) at 150 ºC: reduces pore clogging and can deposit 2-5 wt% boron, depending on flow (6-23 cm^3/s) and pressure (1.2-2.5 bar total; 0.2-0.3 bar $B_{10}H_{14}$)
- Low flow and low pressure: increase of B conc. 10-fold compared to no flow

Accomplishments and Progress

Boron doping II—Deoxygenation of precursors, XPS spectra

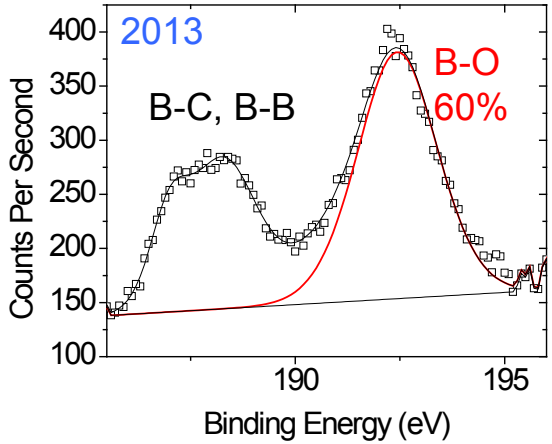
- Residual O in precursor (undoped carbon) competes with C for B: formation of B-O bonds ("boron traps") instead of B-C bonds
- Remove O by high-temp./chem./… treatment before doping
- O removal reduces surface area (graphitization, loss of high-binding-energy defects)
- Optimum treatment, 800 ºC: 4 at% O and Σ= 2500 m^2/g

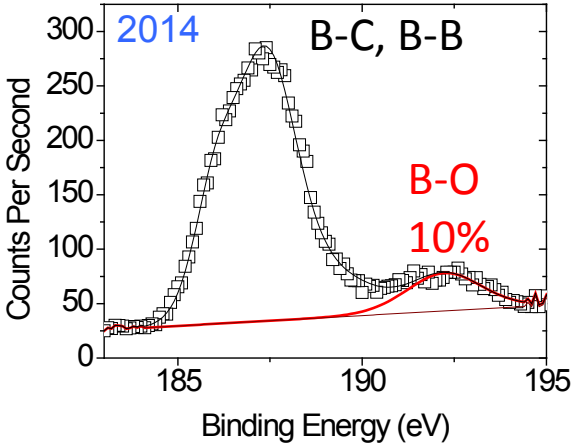




Boron XPS spectra of doped materials:

- Precursor treated at 600 ºC (2013)
- Precursor treated at 1200 ºC (2014)

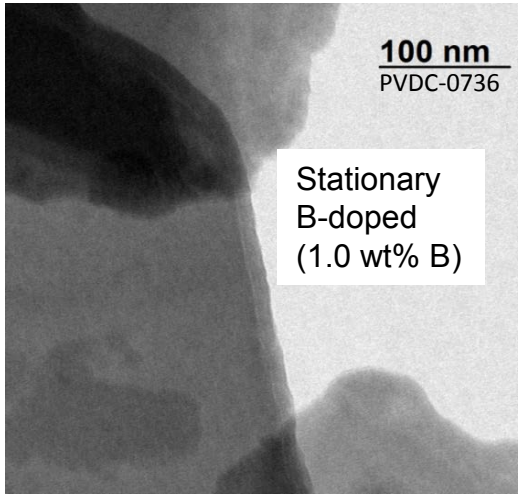




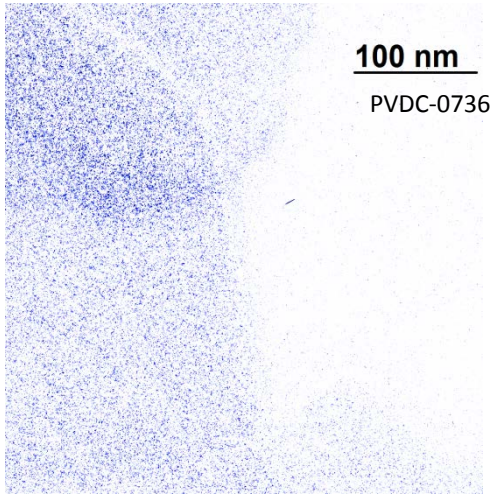
- Deoxygenation at 1200 ºC prior to doping reduced B-O bonds from 60% to 10%
- Successful elimination of boron traps while maintaining high surface area
- For resolution of B-C, B-B (not done here), see slide 12

Accomplishments and Progress

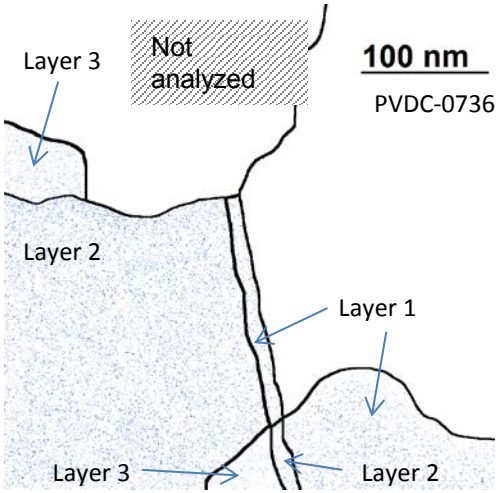
Boron doping III—Uniform boron deposition



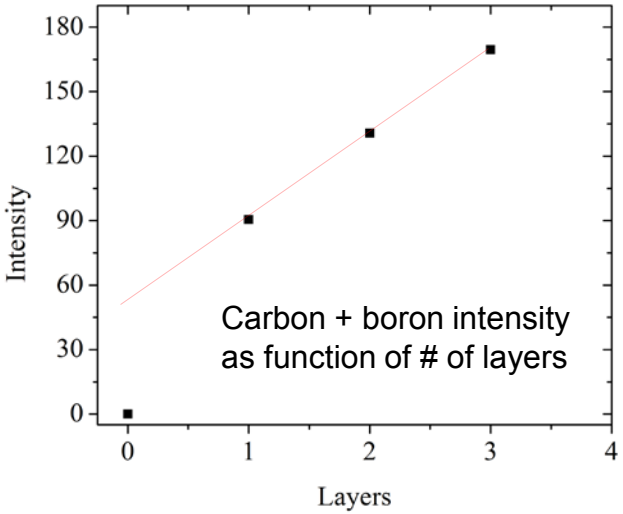
TEM, carbon + boron (zero-loss image)
FEI Tecnai F30 G2 Twin, U. Missouri

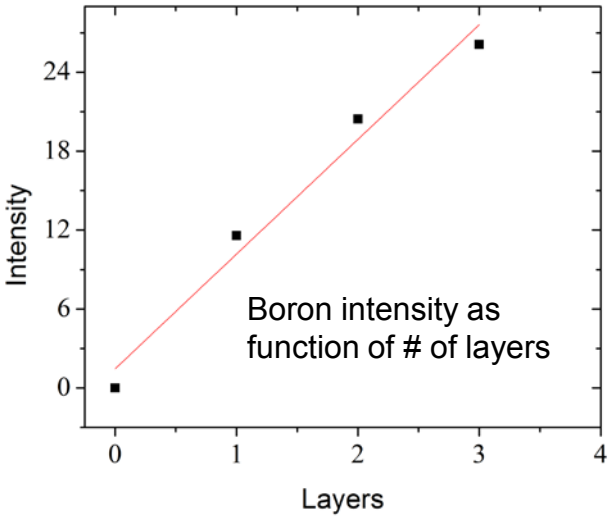


Energy-filtered TEM: boron only (blue)



Energy-filtered TEM: boron (blue), divided by # layers

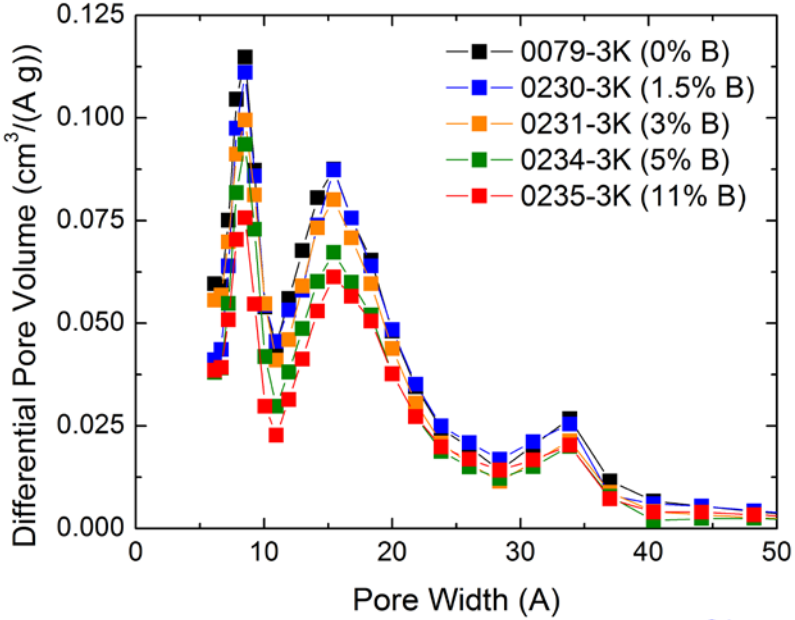


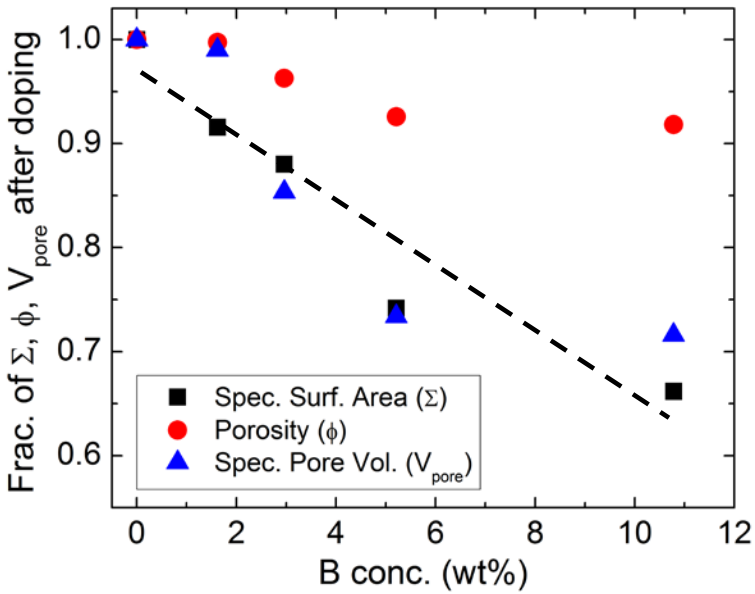


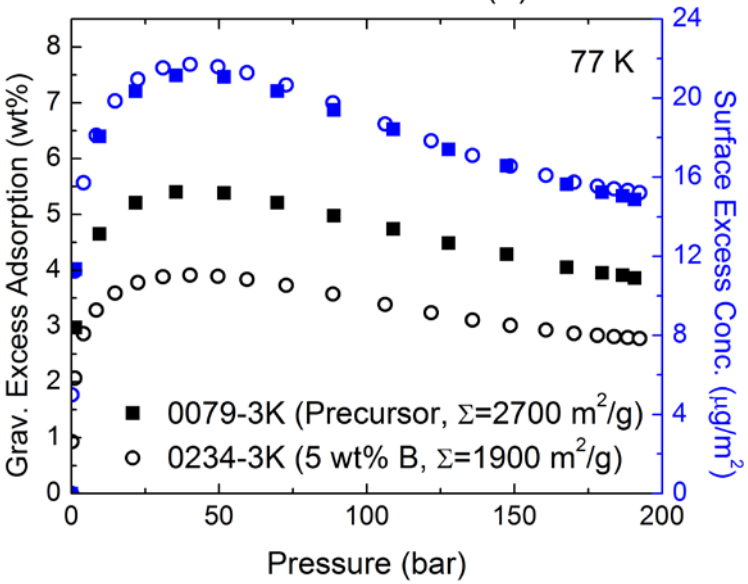
Conclusion: B distributed uniformly over >200 nm laterally and ≥3 graphene layers vertically

Accomplishments and Progress

Boron doping IV—Surface morphology vs B conc. (flow doping)





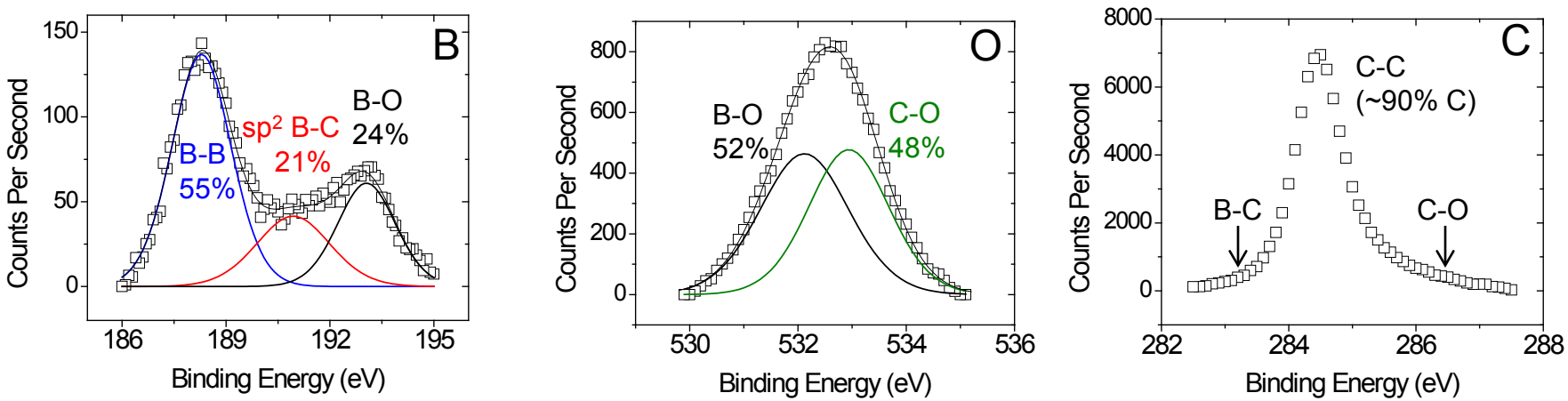


- Increase in B conc. reduces pore volume and surface area, with largest effect in smallest pores (<15 Å). Porosity decreases to a lesser extent
- Increase in B conc. reduces Σ approximately linearly
- Reduction of Σ reduces H_2 grav. excess adsorption in accordance with Chahine's rule
- Identical surface excess conc. (G_{exc}/Σ) indicates identical average H_2 binding energy in doped and undoped samples

Technical Accomplishments

Boron doping V—sp^2-bonded boron in doped materials

XPS spectra of sample 5K-0215 (deoxyg. & annealed at 1200 ºC)



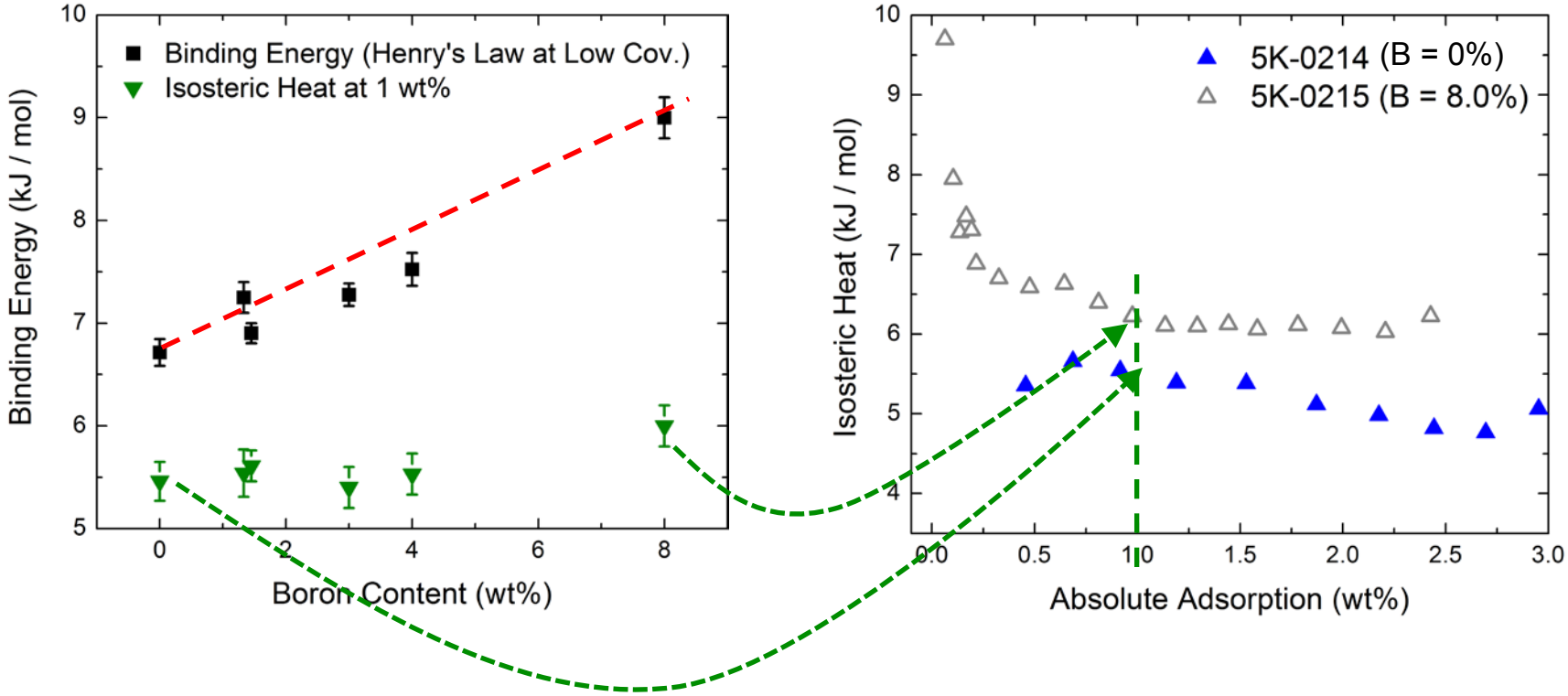
- Achieved: 1-2 wt% sp^2-bonded B (B-C bonds), out of total of 6-14 wt% B
- Best % of sp^2-bonded B: annealing at 1200 ºC
- No significant variation of ΔH_{ads} at high coverage for varying B_{B-C}% (see also next slide)
- Successful deconvolution of B-C and B-B spectrum by analysis of B-O and C-C spectrum
- Side result: final O is ~50% in C-O and ~50% in B-O

Absolute and relative fraction of sp^2-bonded B

Sample	B (wt%)	B_{B-C} (wt%)	$\frac{B_{B-C}}{B}$ (%)	$\Delta H_{ads,\ high\ cov}$ (kJ/mol)
3K-0211	6	0.9	13	5.6 (±0.2)
3K-0205	10	1.1	14	5.5 (±0.2)
3K-0208	14	1.5	13	5.4 (±0.2)
5K-0215	8	1.7	21	6.2 (±0.4)

Accomplishments and Progress

Boron doping VI—H_2 binding energy vs B concentration

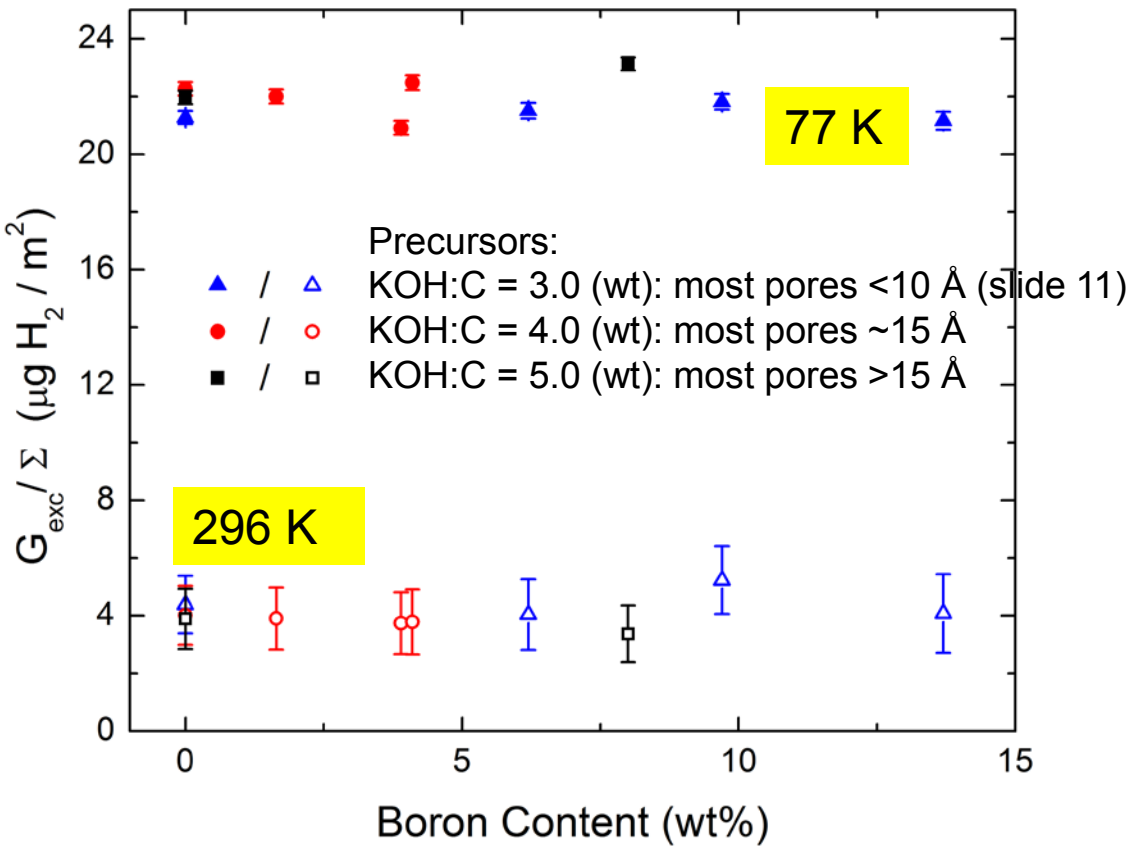


- Binding energies, E_B, from Henry's law (slide 26) increase linearly with boron wt%: 6.7– 9.0 kJ/mol. Demonstrates increase of fraction of high-binding-energy sites
- Isosteric heats, ΔH, from high H_2 coverage (isosteres, slide 26) increase insignificantly with B wt%: 5.5-6.0 kJ/mol. Indicates insignificant increase of average binding energy, $E_{B,av}$
- For 5K-0215: ΔH_{doped} 10-80% higher than $\Delta H_{undoped}$: high binding energies also from ΔH
- For 5K-0215: $\Delta H_{doped,\ zero\ cov}$ = 9.7 kJ/mol agrees well with E_B = 9.0 kJ/mol

Accomplishments and Progress

Boron doping VII—H_2 adsorption on doped materials

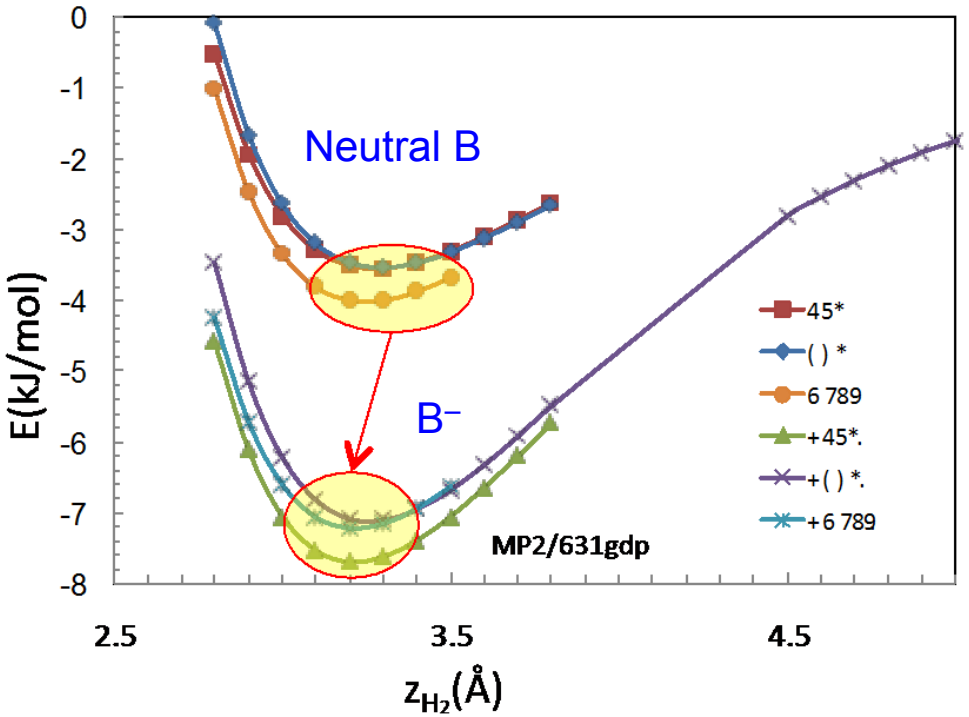
- Screened B-doped materials for high grav. excess ads. per unit surface area
- At 77 K: G_{exc} at local max. (p ~ 50 bar, high coverage)
- At 296 K: G_{exc} at p = 10 bar ("low" coverage)
- Expect G_{exc}/Σ high for high average binding energy, $E_{B,av}$ (departure from Chahine rule)

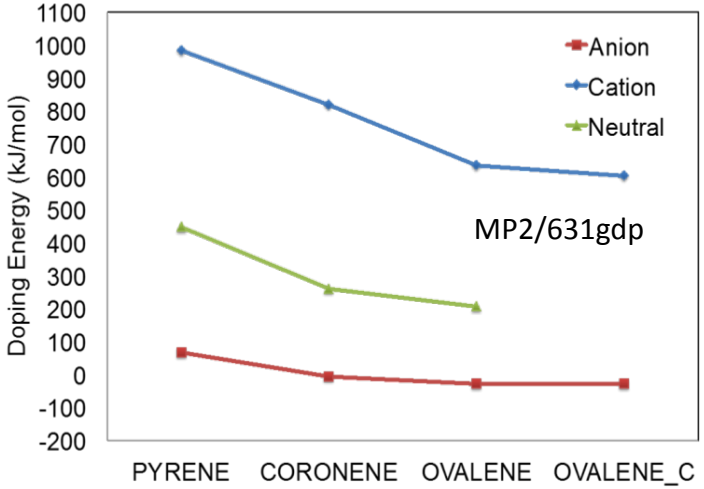


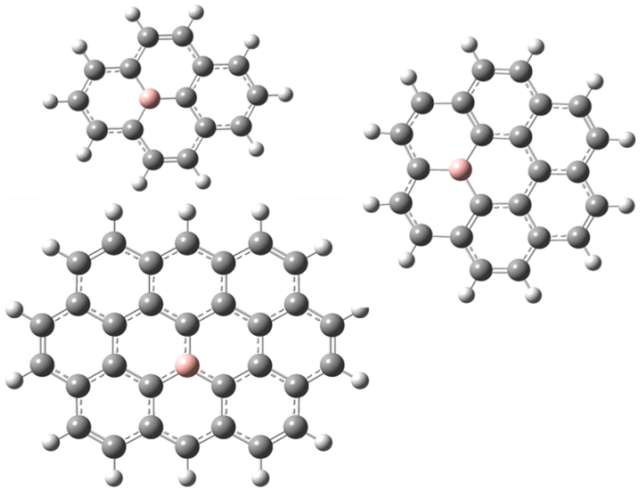
- No significant variation of G_{exc}/Σ with increasing boron content
- Reason I: Fraction of high-binding-energy sites too small to raise $E_{B,av}$ (slide 13)
- Reason II: Not all B in doped material is sp^2-bonded, high-E_B boron (slide 12)

Accomplishments and Progress

Does B⁻ host higher binding energy than neutral B?







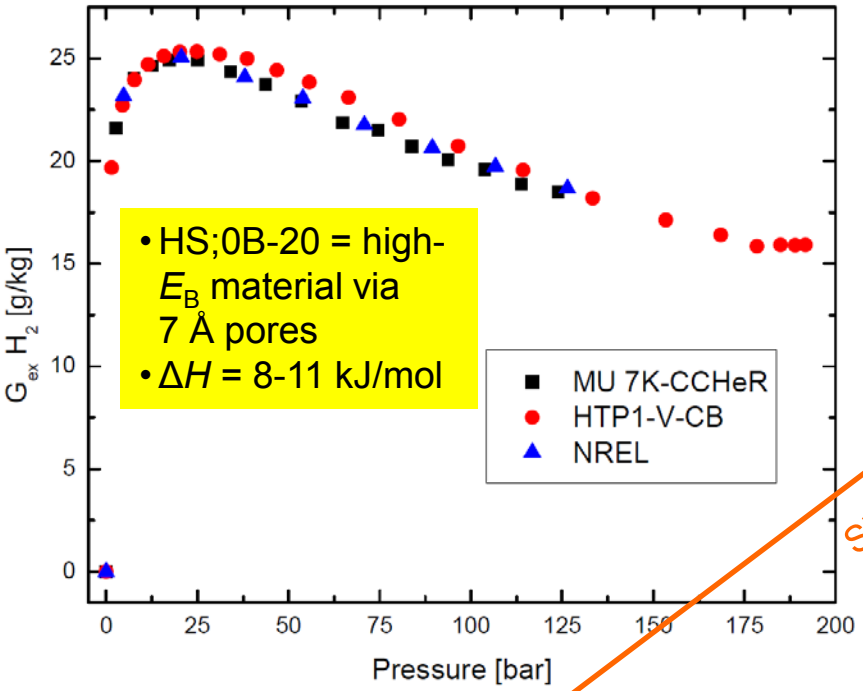
- Yes—neg. charge creates larger polarization of H_2
- H_2 on B-doped C: anionic B-doped C shows enhancement 4-5 → 7-8 kJ/mol.
- 50% of the enhancement attributable to electrostatic field due to charge distribution near B

*Calculated using MP2/631gdp method: "2nd Order Moller-Plesset" 631gdp is the basis set

Accomplishments and Progress

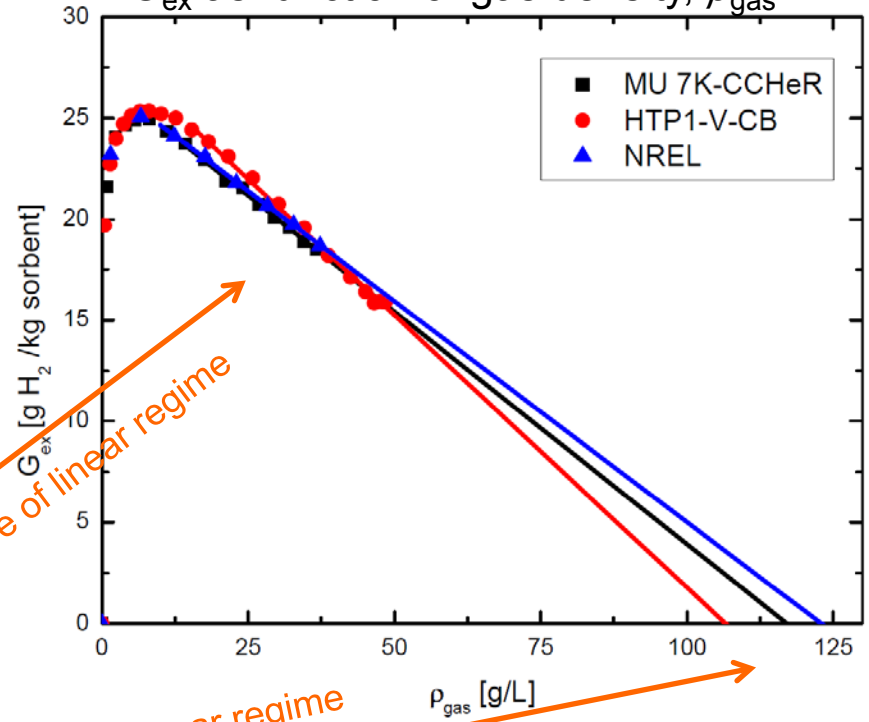
Validation of U. Missouri data by NREL: synthetic carbon HS;0B-20

G_{ex} as function of gas pressure, p



- HS;0B-20 = high-E_B material via 7 Å pores
- ΔH = 8-11 kJ/mol

G_{ex} as function of gas density, ρ_{gas}



Slope of linear regime

Intercept of linear regime

$$G_{ex} = (V_{film}/m_{solid})\,[\rho_{film} - \rho_{gas}]$$

$$G_{ex} = (V_{film}/m_{solid})\,[\rho_{film,sat} - \rho_{gas}]$$

V_{film} = const, $\rho_{film,sat}$ = const

	$\rho_{film,sat}$	V_{film}/m_{solid}	V_{film}/V_{pore}
HTP1-V-CB	106 g/L	0.27 cm^3/g	0.63
MU 7K-CCHeR	117 g/L	0.23 cm^3/g	0.53
NREL	122 g/L	0.22 cm^3/g	0.51

- Film density over 50% higher than liq. H_2 (71 g/L)
- Film volume ≠ total pore volume!

Responses to Previous Year's Reviewer Comments

- FY13 Reviewer Comment: Focus on understanding the nature of the boron doping and its impact on enhanced hydrogen storage is important; abilities of these materials to achieve DOE targets was not apparent. This should be a focus of any future work.
- Response: Development of a boron doped material with binding energy > 10 kJ/mol would lead to materials which meet 2017 DOE onboard storage targets (0.055kg H_2/kg system and 0.04 kg H_2/L system) (see slides 3 & 4).
- FY13 Reviewer Comment: There are still unresolved questions regarding the most basic features of the materials, such as what the composition and local structure. If the fundamentals of the material are still not understood, it is unclear why researchers would scale up to monoliths
- Response: The presence of sp2 B-C bonds and their concentration, and B-B bonds and their concentration is reported in slide 9. Uniformity of B concentration in C has been established in slide 10. Doping of monoliths has been discontinued in favor of systematic studies of B-doping of powder materials (DOE redirection January/2014)
- FY13 Reviewer Comment: Incorrect assumptions about the core possibilities associated with boron-doping levels in a carbon matrix (e.g., 20% brings one to boron-carbide)
- Response: There is ample experimental evidence in the literature for high B concentrations in sp^2 B-C substitutional compounds (up to 25% in BC_3). Boron-carbide starts at 80%, not 20% (see slide 7).

Collaborations (2013-2014)

Institution/Collaborators	Role
NREL (Federal laboratory): P. Parilla, T. Gennett	Validation of H_2 sorption isotherms
NIST Center for Neutron Research (Federal laboratory): R. Paul	PGAA on boron-doped carbons
ORNL (Federal laboratory): R. Olsen J. Idrobo	High-density H_2 films Ultrahigh-resolution TEM and EELS
U. Missouri (University): M. Greenlief T. White, W. Ritts H. Foley	XPS analysis Energy-filtered TEM and EELS Boron-doped nanoporous carbons
Missouri U. of Science & Technology (University): D. Waddill	XPS analysis
U. Missouri-Kansas City (University)**:** P. Rulis	Modeling of XPS and EELS spectra
OsComp (Industry): J. Romanos	Monolith fabrication, high-density H_2 films
MeadWestvaco (Industry): B.-P. Holbrook	Industrial scale production of nanoporous carbon

Proposed Future Work (Plans Through 11/2014)

- Utilize computational analysis to quantify perturbations to the 1s electron orbitals in sp^2 B-C bonds. This will increase our understanding of the B-C bonds present in our materials via XPS data.
- Collect NMR data on boron doped nanoporous carbons to further establish the presence of sp^2 boron carbon bonds.
- Optimize vapor deposition/decomposition of $B_{10}H_{14}$ and annealing of B to insure boron is uniformly deposited and incorporated into carbon lattice.
- Establish maximum boron content that yields increase in isosteric heat at low coverage.
- Establish that increases in isosteric heat from boron doping enhance hydrogen uptake.

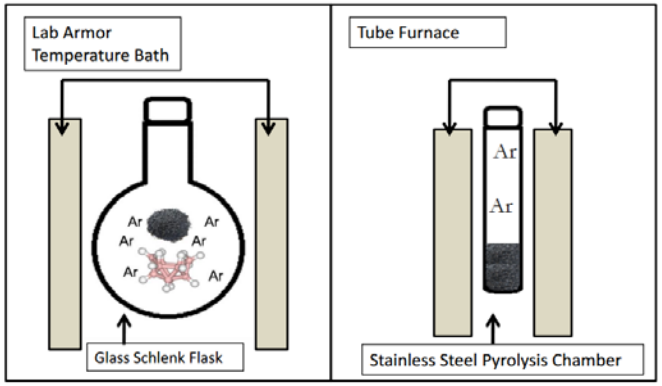
Project Summary

Relevance	The boron-doped carbons developed in this project have the potential to meet the 2017 onboard hydrogen storage goals established by the DOE by creating adsorbents with high binding energies and high surface areas.
Approach	We first create undoped high-surface-area materials; then dope with boron by deposition and decomposition of decaborane into elemental boron and hydrogen, followed by incorporation of boron atoms into the carbon lattice.
Technical Accomplishments	Established protocols for reproducible incorporation of 1-15 wt% boron into high-surface carbons, with a ratio of B-C to B-B bonds of 0.25-0.33. Established presence of binding energies of 5-10 kJ/mol for B:(B+C) = 0-8 wt%, and 7-11 kJ/mol for undoped synthetic carbons, both at low H_2 coverage.
Proposed Future Work	Improve B incorporation into carbon, with a larger ratio of B-C to B-B bonds, for achievement of ≥10 kJ/mol binding energy at low and high H_2 coverage.

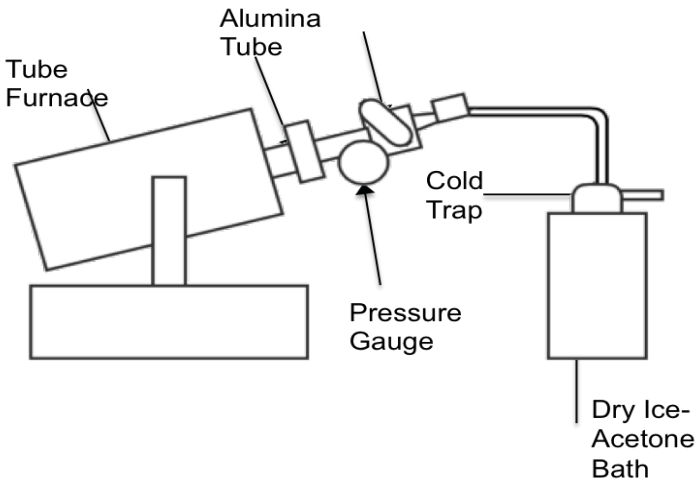
Technical Back-Up Slides

Boron-doping instrumentation

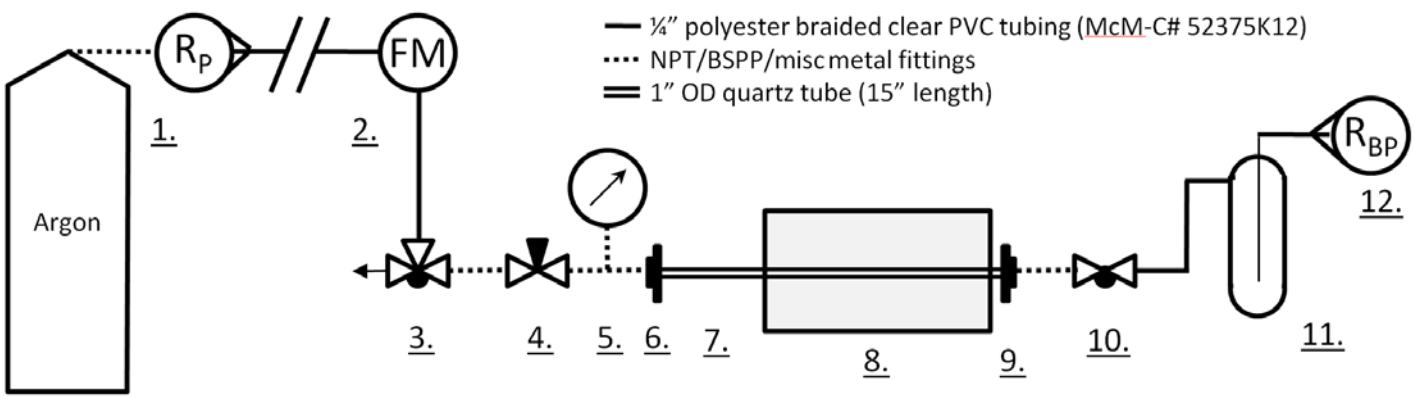
2-step stationary (1. deposition, 2. pyrolysis; DB/C mixed), x/10-4/13



1-step stationary (combined deposition/pyrolysis; DB/C mixed), 5/13-present

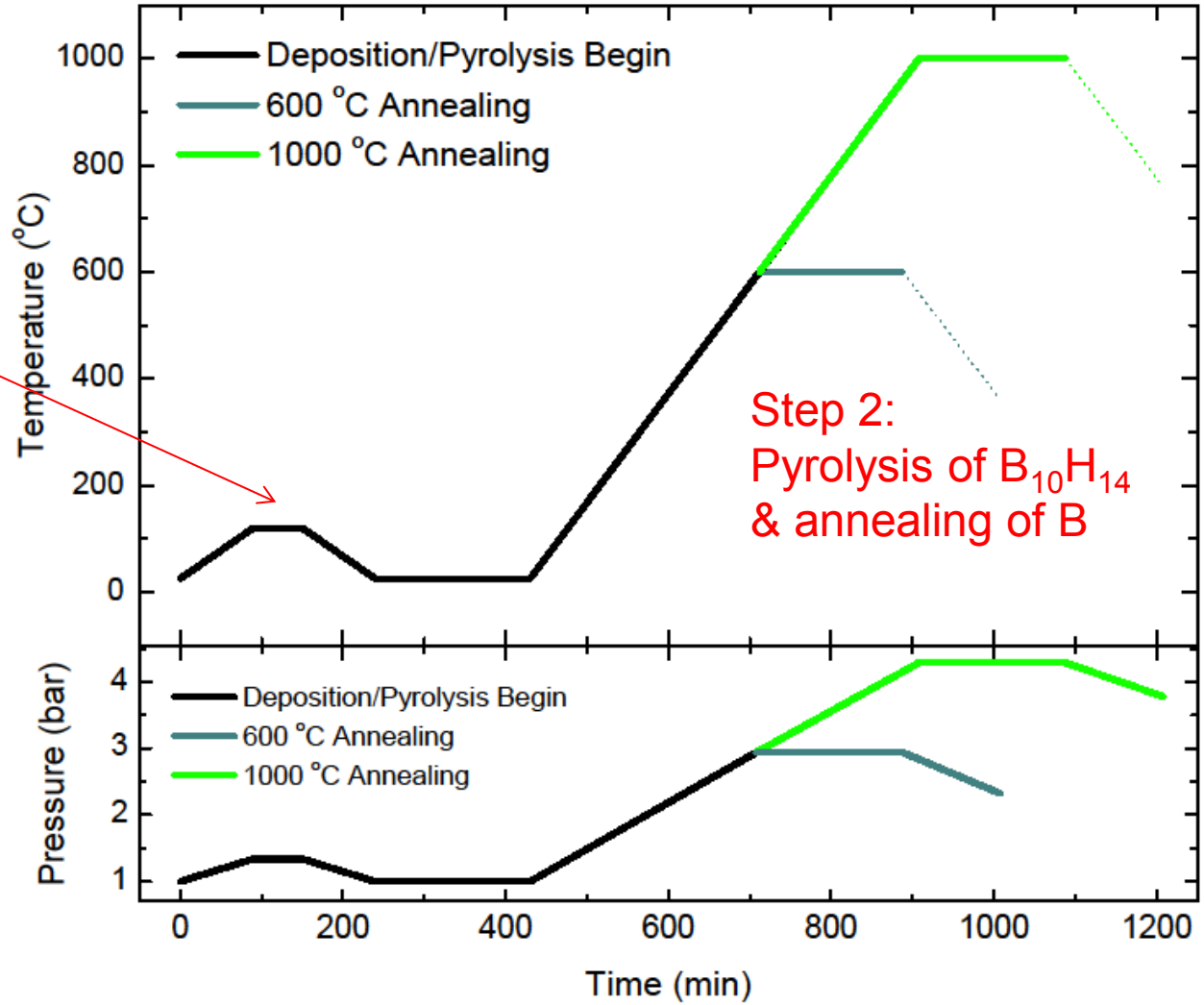


2-step continuous-flow (1. deposition, 2. pyrolysis; DB/C separate), 12/13-present



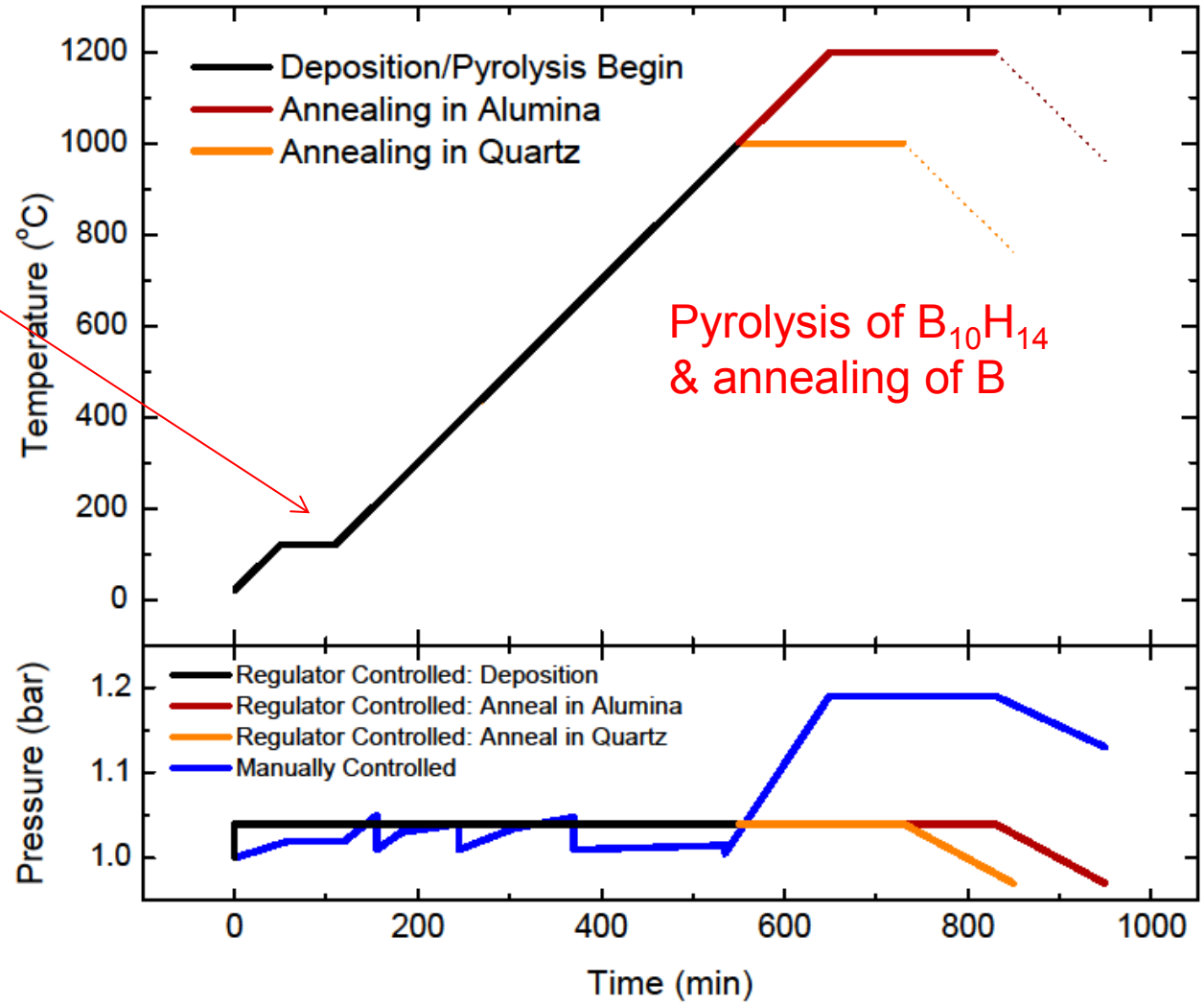
T, *p*-profile for 2-step stationary doping

Step 1:
C +
$B_{10}H_{14}$(liq/gas)



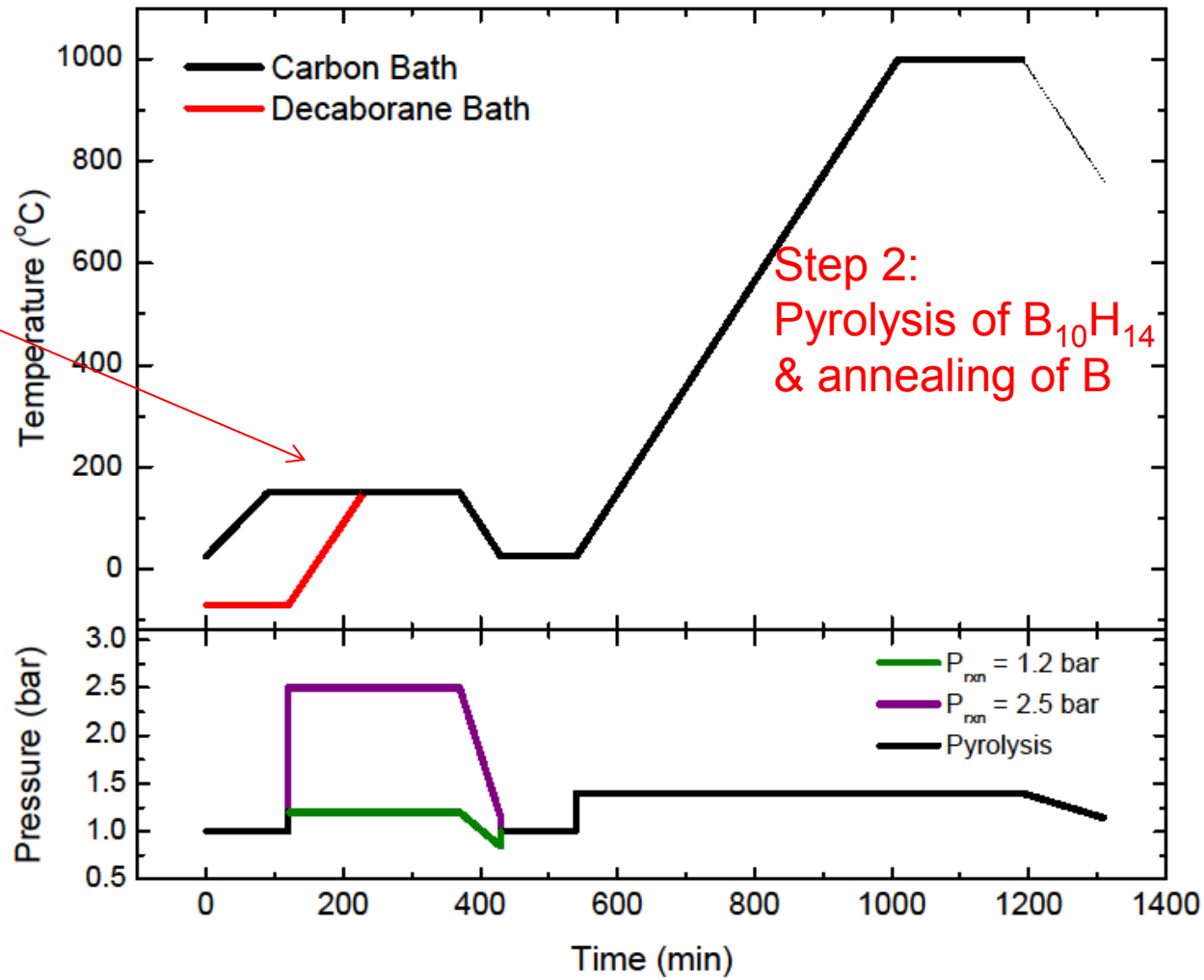
T, *p*-profile for 1-step stationary doping

C +
$B_{10}H_{14}$(liq/gas)



T, *p*-profile for 2-step continuous-flow doping

Step 1:
C + $B_{10}H_{14}$(gas)



Binding energies from Henry's law, isosteric heats from isosteres

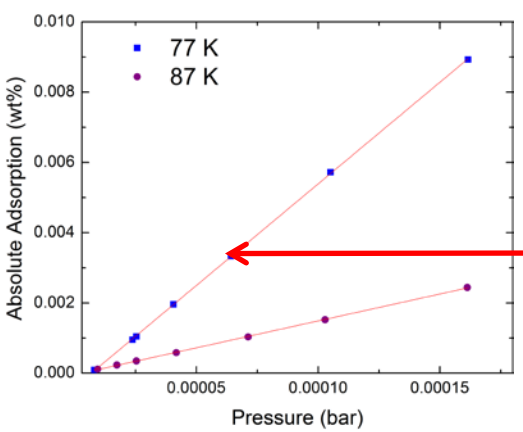
Henry's Law Method:

- Most methods of determining E_B proceed via ΔH and depend on film thickness (t_f) assumptions.
- E_B from Henry's law are independent of film thickness.
- Langmuir model of mobile adsorption (L.P. limit)
- E_B calc. from k_H using isotherms at two different temperatures:
- Resembles Clausius Clapeyron Equation
- Most methods of determining

$$\frac{m_{\text{abs}}}{m_{\text{s}}} = \frac{\sum M_{\text{gas}}}{\alpha(T) N_{\text{A}}} \theta(p,T) \longrightarrow \frac{m_{\text{ads}}(p,T)}{m_{\text{s}}} = k_{\text{H}}(T) p$$

$$e^{\frac{E_{\text{B}}}{N_{\text{A}} k}\left(\frac{T_2 - T_1}{T_1 T_2}\right)} = \frac{k_{\text{H}}(T_1)}{k_{\text{H}}(T_2)} \sqrt{\frac{T_1}{T_2}}$$

$$\boxed{E_{\text{B}} = N_{\text{A}} k \left(\frac{T_1 T_2}{T_2 - T_1}\right) \ln\left[\frac{k_H(T_1)}{k_H(T_2)} \sqrt{\frac{T_1}{T_2}}\right]}$$



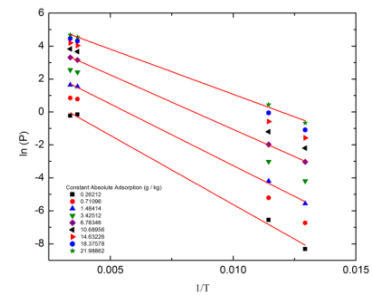
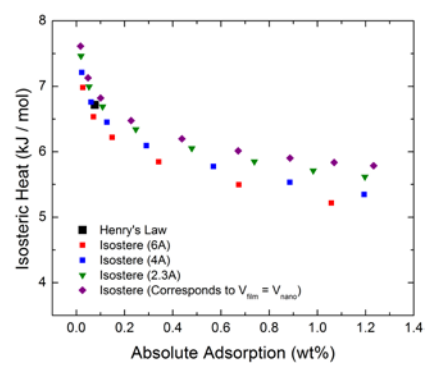
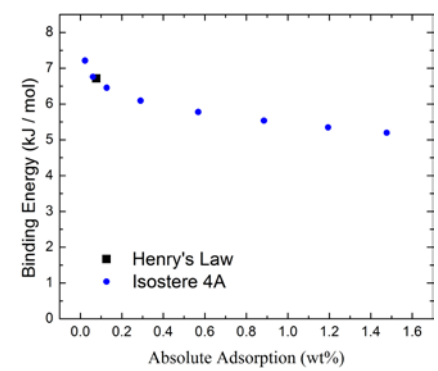
Slope of the adsorption function is the Henry's law constant. Henry's law is observed here

$$k_{\text{H}}(T) = \frac{\chi(T, E_{\text{B}}) m \sum}{\alpha(T)}$$

Method of Isosteres:

- Convert to Absolute Adsorption
- Solve for pressure at constant coverage
- Using rearrangement of C.C. equation
- ΔH solved from slope
- Assumes negligible changes in ΔH with temp.
- Choose V_{film} so that isostere matches E_B from Henry's

$$\frac{m_{\text{abs}}}{m_{\text{s}}} = \frac{m_{\text{exc}}}{m_{\text{s}}} + \rho_{\text{gas}}(p,T) V_{\text{film}}$$

$$\Delta_{ads} H(\theta) = -R \left(\frac{\ln[P_1(T)] - \ln[P_2(T)]}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}\right)$$

$$\ln[P(T)] = \frac{\Delta_{ads} H(\theta)}{R} \left(\frac{1}{T}\right)$$