Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Overview

Timeline

- Project start date:
  - September 1, 2008
- Project end date:
  - November 30, 2013
- Percent complete: 75%

Barriers

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

Budget

- **Total project funding**:
  - DOE share: $1,899K
  - Contractor share: $514K
- **Funding for FY 2011**
  - DOE share: $340K
  - Contractor share: $125K
- **Funding for FY 2012**
  - DOE share: $214K
  - Contractor share: $145K (est.)

Partners

- L. Simpson, P. Parilla, K. O'Neill - NREL
- J. Ilavsky - Advanced Photon Source, ANL
- C. Brown, J. Burress - NIST
- L. Firlej - U. Montpellier II, France
- B. Kuchta - U. Marseille, France
- S. Roszak - Wroclaw U. Technology, Poland
- H. Taub - U. Missouri
- M. Stone - ORNL
- A. Kleinhammes – U. North Carolina

Objectives & Relevance

Fabricate high-surface-area, multiply surface-functionalized nanoporous carbon, from corncob & other precursors, for reversible H_2 storage (physisorption) with superior storage capacity

- Understand mechanisms & optimize procedures for boron doping of activated carbon

Characterize materials & demonstrate storage performance

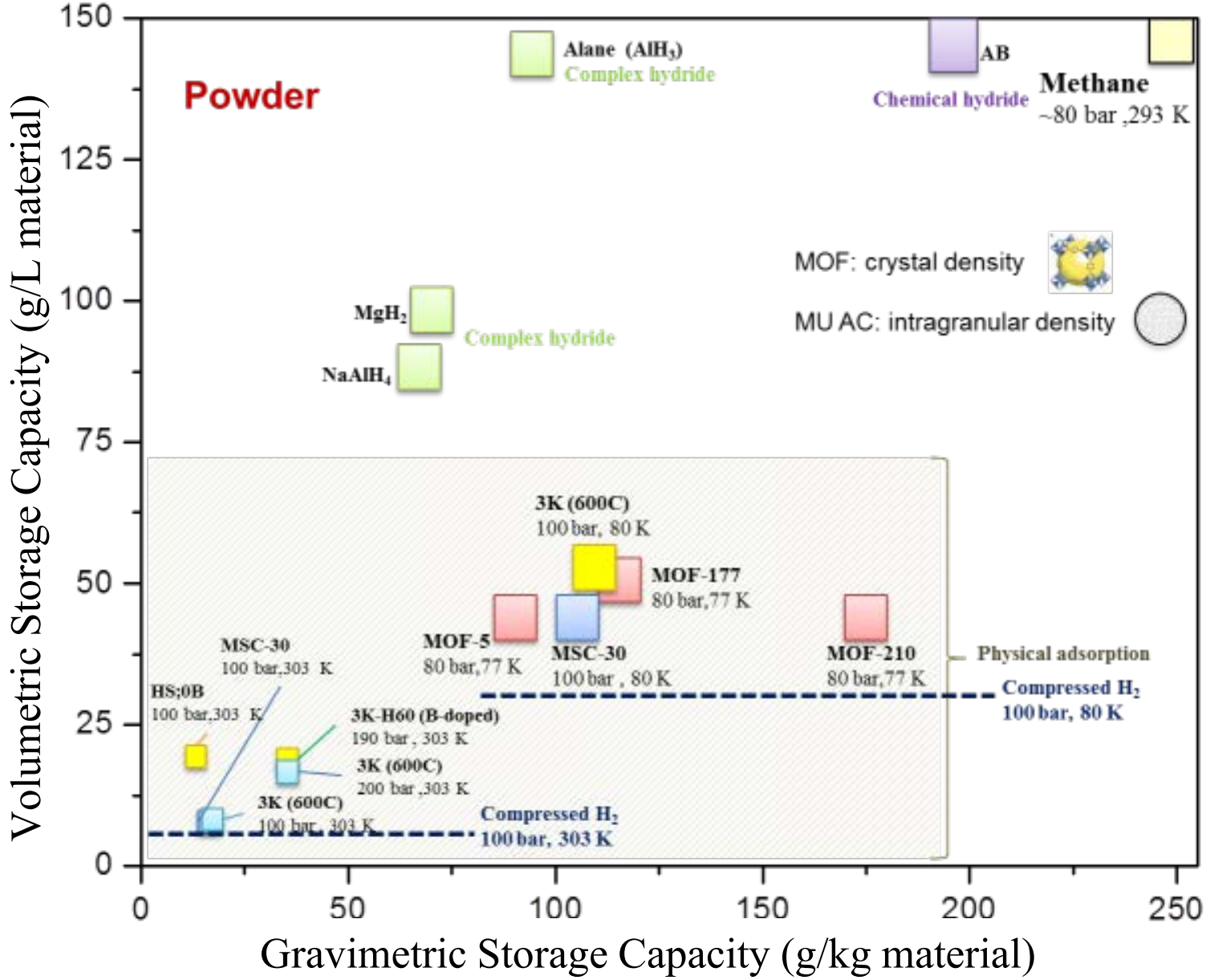
- Determine pore-space architecture, nature of functionalized sites, H_2 sorption isotherms (0-200 bar), isosteric heats, & kinetics, at 77-300 K
- Establish effectiveness of boron functionalization by deposition & pyrolysis of (i) $B_{10}H_{14}$ & (ii) BCl_3
- Establish B-C bonds in B-functionalized materials (FTIR, XPS)
- Establish enhanced binding & adsorption of H_2 on boron-functionalized carbon
- Develop computational predictions of H_2 adsorption for various pore geometries/chemistries

Optimize pore architecture & composition

- Establish optimal precursors for H_2 storage as function of KOH:C ratio & activation temperature
- Compare B-functionalized carbons produced by different synthesis methods

Background

Sorption Landscape



Approach

- Raise binding energy of H_2 on carbon by functionalization of surface with boron
  - Firlej et al., 2009; Kuchta et al., 2010: Binding energy of H_2 on carbon: 5 kJ/mol, on B-substituted carbon: 10-15 kJ/mol
  - Computed H_2 ads. isotherms (GCMC) at 10 wt% B:C: 5 wt% H_2 at 293 K, 100 bar

- (1) Produce high-surface-area carbon, (2) Dope surface with B (> 2000 m^2/g)
  - $B_{10}H_{14}$ (volatile), incorporate B into lattice by thermal annealing
  - Achieved ~ 10% B:C: small reduction in surface area, higher isosteric heat of adsorption, higher excess adsorption at room temperature

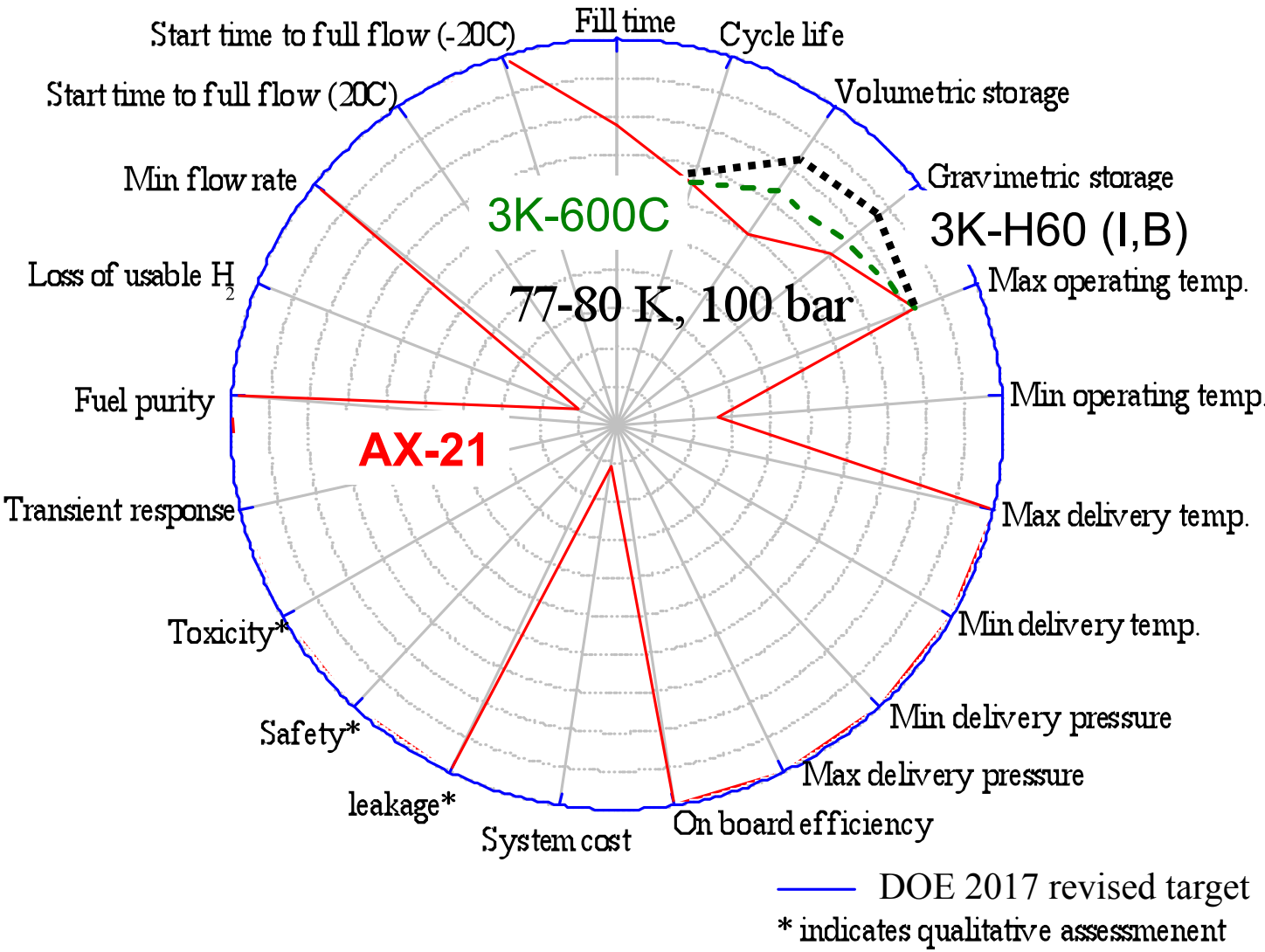
- 10-liter hydrogen sorption tank
  - Flow measurement & control (transport & sorption kinetics, heat management)

- Surface, pore, and chemical characterization of materials
  - GCMC: adsorption in heterogeneous pores, non-traditional pore geometries, etc.
  - SAXS & N2 sorption: characterization of pore geometries
  - FTIR & XPS: characterization of incorporated boron

- Carbon monoliths for increased hydrogen storage
  - Boron-doped monoliths for optimization of gravimetric & volumetric storage capacity

Technical Accomplishments

AX-21, U. Missouri: 3K-600C (0% boron), 3K-H60 (I,B) (7% boron)

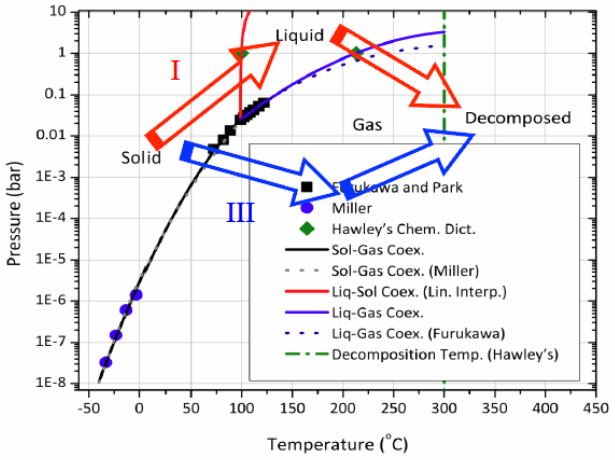


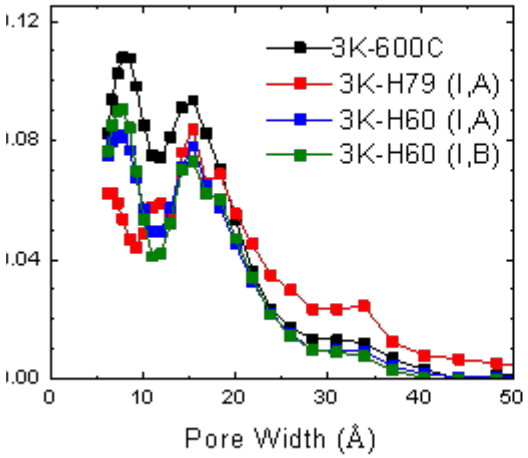
U. Missouri: Projected from experimental values

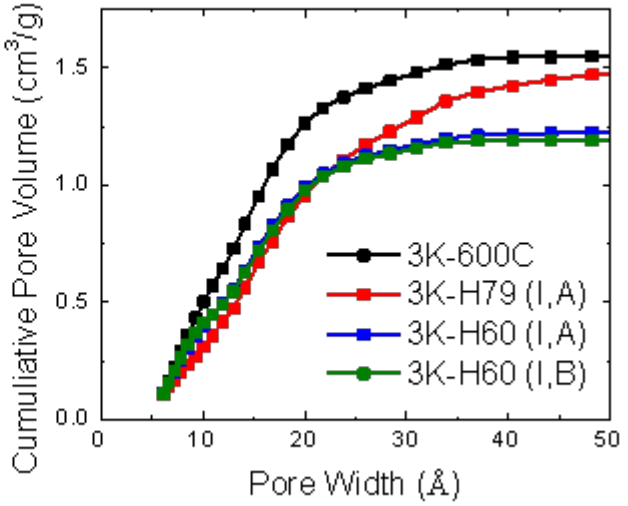
AX-21: Hydrogen storage engineering center of excellence. *Anton. et al.*, 2010-2011 .The gravimetric and volumetric storage capacity of material AX-21 decreased by ~62% and ~44% respectively when including the complete storage system.

Technical Accomplishments

Boron-doped Carbons from $B_{10}H_{14}$ Deposition: Different Synthesis Methods





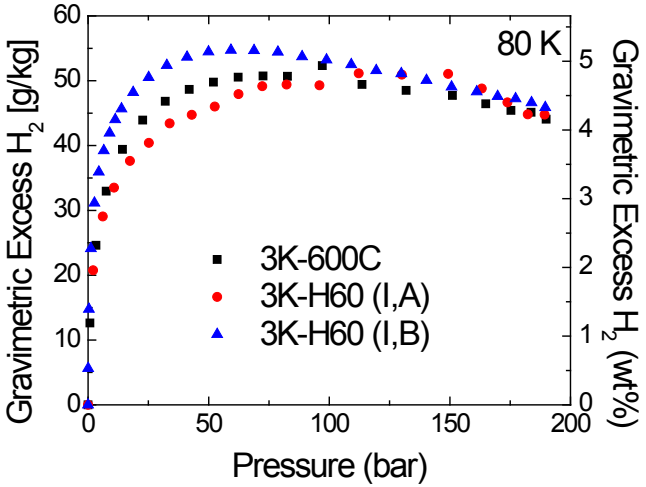


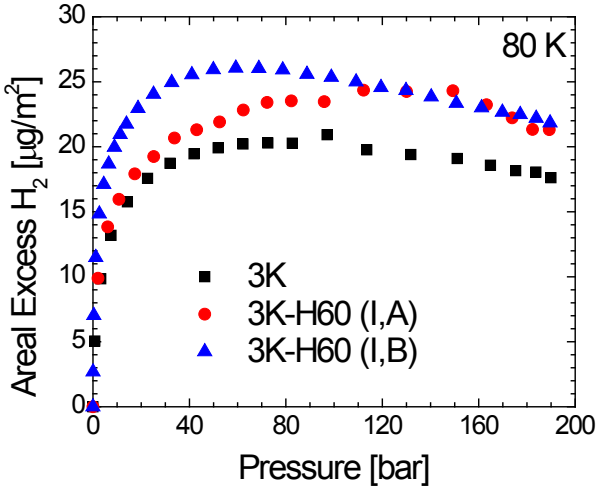
Sample (B-doped: out of 12 samples synthesized 2011-12)	Precursor	B:C %	Σ_{N2} (m^2/g)	Φ_{N2}	Annealing temp.
3K 3/3/10-B	Self	0.0	2700	0.77	N/A
3K 3/3/10-B Outgassed@ 600 °C	Self	0.0	2500	0.76	N/A
3K-H60 (I,A), 1-step doping	3K 3/3/10-B Outgassed@ 600 °C	8.6	2100	0.74	600°C
3K-H60 (I,B), 1-step doping	3K 3/3/10-B Outgassed@ 600 °C	6.7	2100	0.72	1000°C
3K-H79 (I,A), 5-step doping	3K-H78 (I,A)	7.1	2200	0.78	600°C

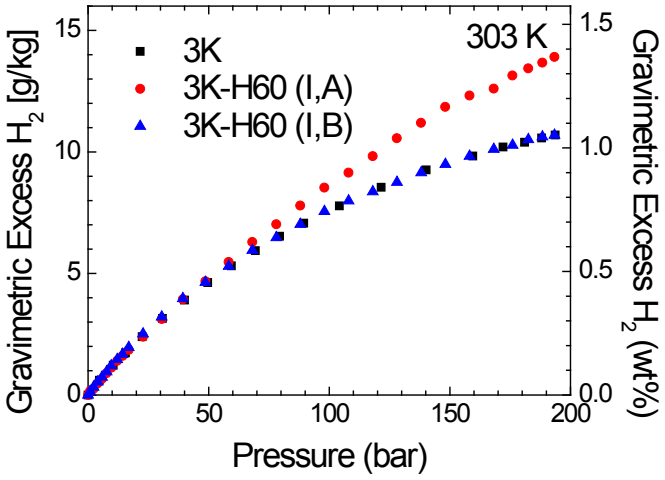
- Achieved ~ 9% B:C, 1-step doping: no significant reduction in surface area (< 15%)
- Achieved ~ 7% B:C, 5-step doping: no significant reduction in surface area (< 15%)
- 5-step doping gives ~ 20% increase in total pore volume vs. 1-step doping
- Annealing at 1000 °C reduces B content by ~ 20%, with unchanged surface area and pore size distribution, loss of B through further decomposion

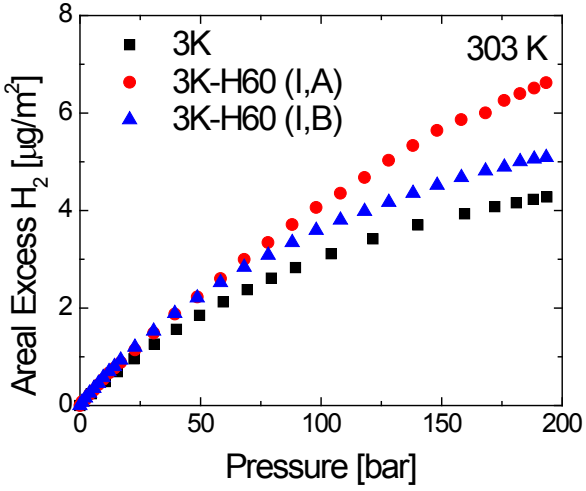
Technical Accomplishments

Hydrogen Sorption on B-doped Samples: Cryogenic and Room Temperature







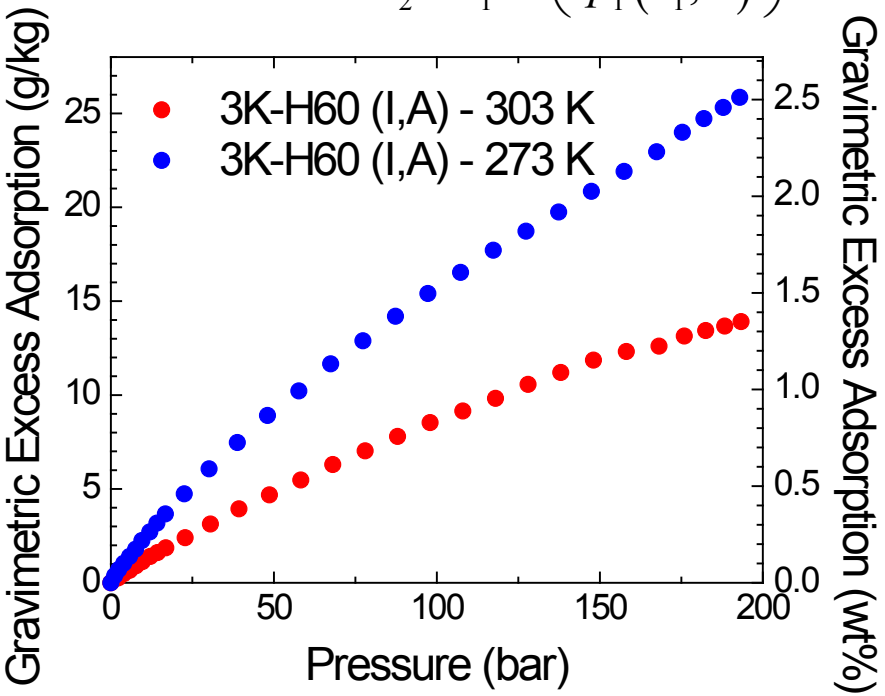


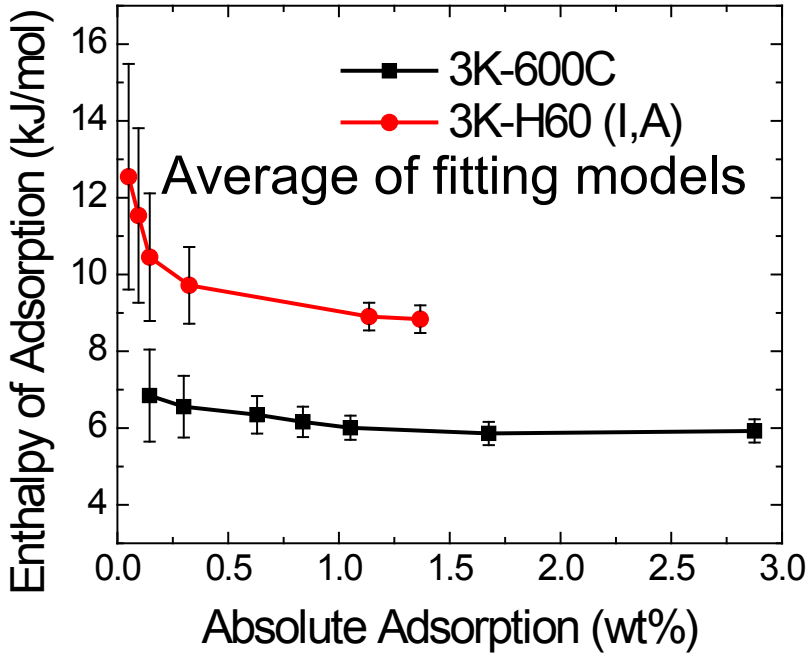
- Systematic increase of H_2 with B:C doping ratio: 3K-H60(I,A) > 3K-H60(I,B) at 303 K
- Enhancement at high *T*, *P*: increase in *average* binding energy
- At 80K: 3K-H60(I,A) was exposed to oxygen before analysis, hence lower uptake than 3K-H60(I,B); but still better than 3K

Technical Accomplishments

Enhanced Isosteric heats for B-doped carbon

$$\Delta_{ads}H(\theta) = R\frac{T_1T_2}{T_2 - T_1}\ln\left(\frac{p_2(T_2,\theta)}{p_1(T_1,\theta)}\right),$$ Clausius-Clapeyron equation

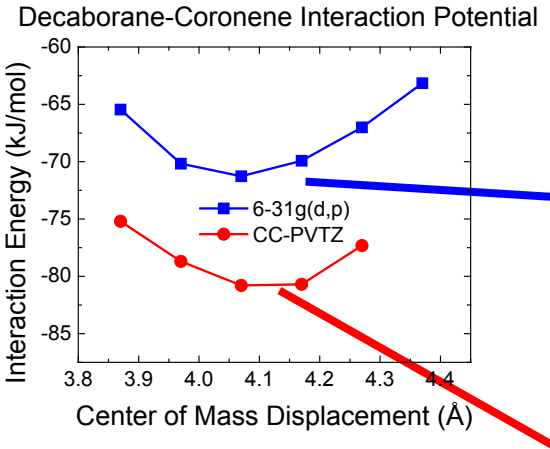




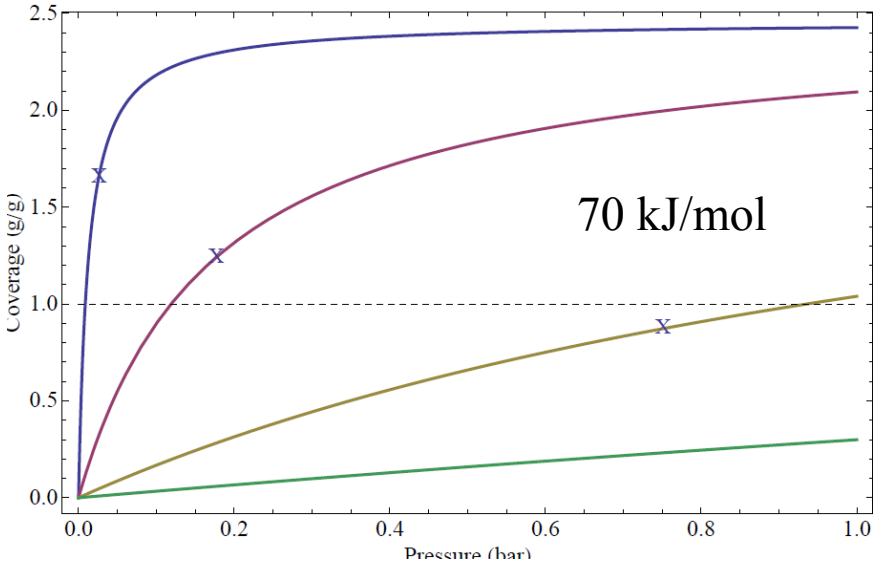
- B-doped materials increase binding energy from ~6 kJ/mol to ~10 kJ/mol
- Enhanced Δh, similar to our theoretical predictions (2009-2010)
- Absolute isotherms used [see 2011 AMR]
- 273 K has 80% higher excess adsorption than 303 K; doubling of binding energy results in quadratic increase in adsorption, in Henry's law regime, as temperature decreases

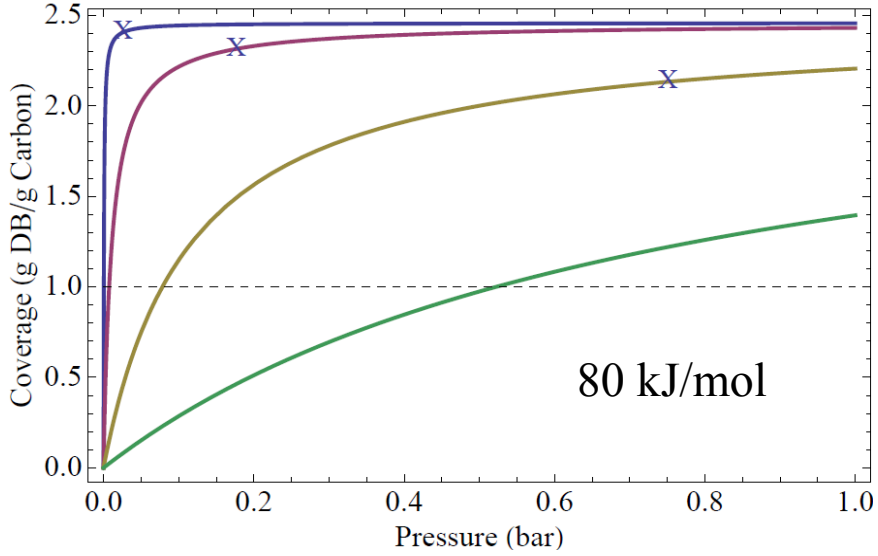
Technical Accomplishments

Decaborane Deposition at Low Vapor Pressure



$$\theta = \frac{p_{\text{vapor}}\chi_{\text{DB}}}{1 + p_{\text{vapor}}\chi_{\text{DB}}} \qquad \chi_{\text{DB}} = \frac{\exp\left[E_{\text{B}}/kT\right]}{\Pi_{i=1}^{3}\sinh\left(\frac{h\nu_i}{2kT}\right)}\sqrt{\frac{h^6}{\left(8\pi M_{\text{DB}}\right)^3\left(kT\right)^6}}$$



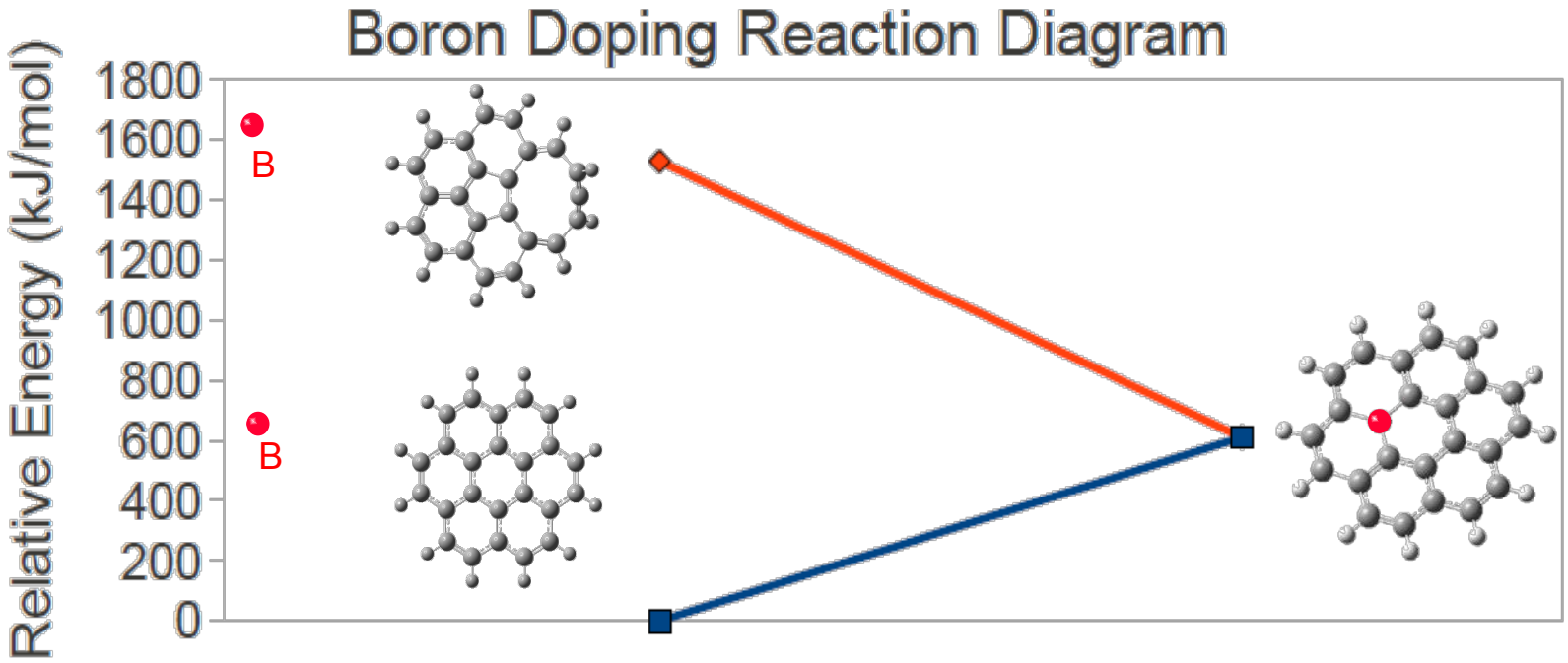


- Langmuir isotherms at T=100, 150, 200, 250 C (blue, red, gold, green)
- 'X's mark decaborane vapor pressures at respective temperatures

- Lower (upper) bound on binding energy suggests 10% coverage achievable without pore blockage for T < 150 C ($T<T_{\text{decomposition}}$)
- Experimental pressures and temperatures close to computational optimum

Technical Accomplishments

Boron Incorporation into Carbon Lattice

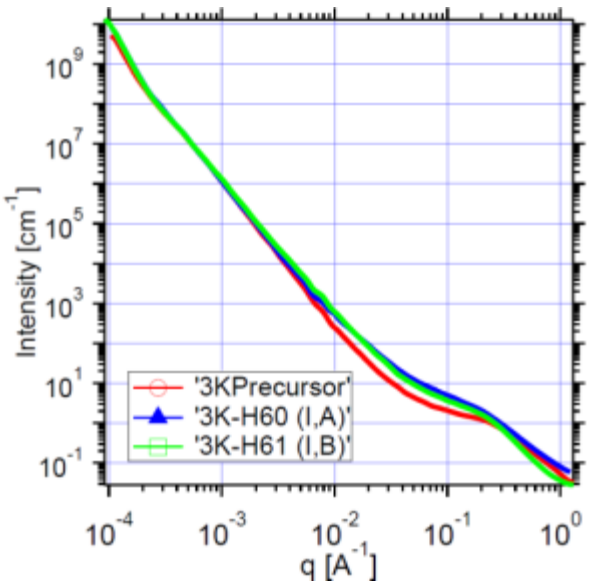


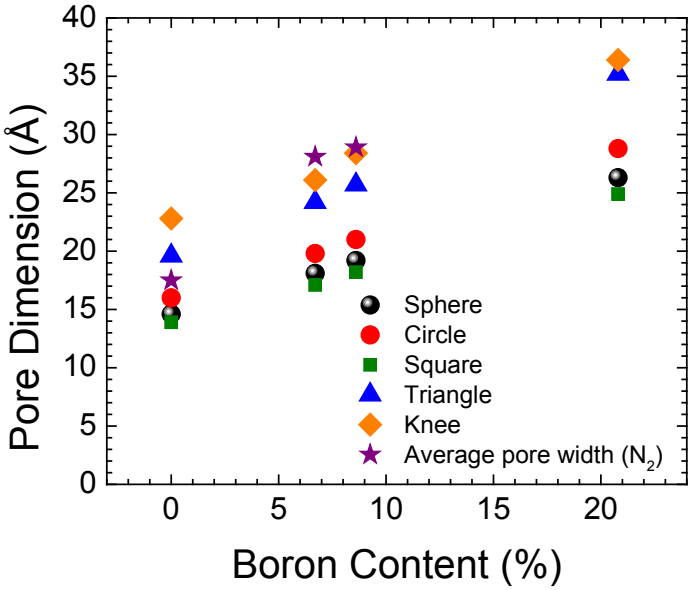
- During annealing, decaborane will decompose into a plasma of boron ions
- Large amount of energy required to directly replace a carbon with boron ($\Delta E \approx$ 600 kJ/mol)
- Activated carbon is comprised of loose flakes of likely defective graphene

- If a defect is already present, carbon structure readily incorporates boron ($\Delta E \approx -1000$ kJ/mol)

Technical Accomplishments

Small Angle X-ray Scattering





- Boron doping has minimal effect at large length scales
- $q < 3\text{x}10^{-3}$ Å^{-1}: surface fractal network with $D_s \approx 2.5$
- $q > 0.3$ Å^{-1}: modeled with Guinier fit to determine radius of gyration

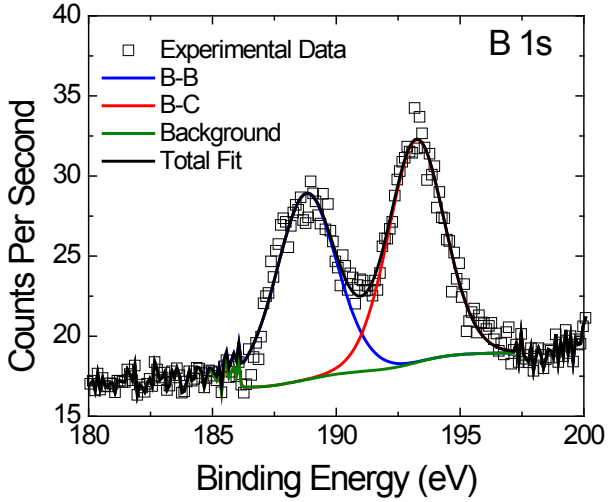
Model	3K-600C	3K-H60 (I,A)	3K-H60 (I,B)	3K-H63 (I,A)
Boron content (%)	0 %	9 %	7 %	21 %
Radius of gyration	6 Å	7 Å	7 Å	10 Å
Side length square cross section pore, from R_G	14 Å	18 Å	17 Å	25 Å
Ave pore width (SAXS, knee)	23 Å	28 Å	26 Å	36 Å
Ave pore width (N_2 sorption)	18 Å	29 Å	28 Å	N/A

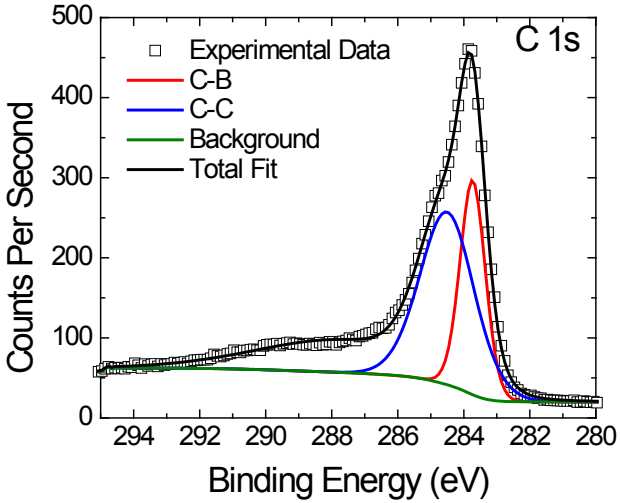
- Radius of gyration and resulting average pore widths increase linearly with boron content
- Consistent with reduction in pore volumes of narrowest pores

Technical Accomplishments

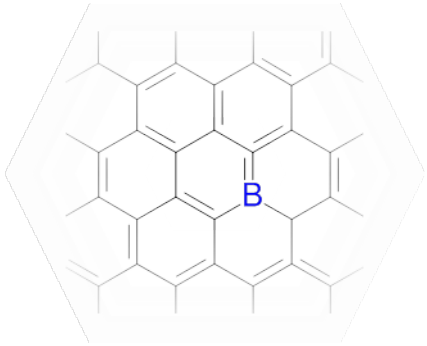
X-ray photoelectron spectroscopy

- ~50% of the boron in sample is bound to a carbon.
- Main carbon peak resolved into two component peaks with energies characteristic of C-B and C-C bonds.
- 26% of carbon being in a C-B bond is consistent with ~8% boron where boron has displaced a carbon in hexagonal lattice.





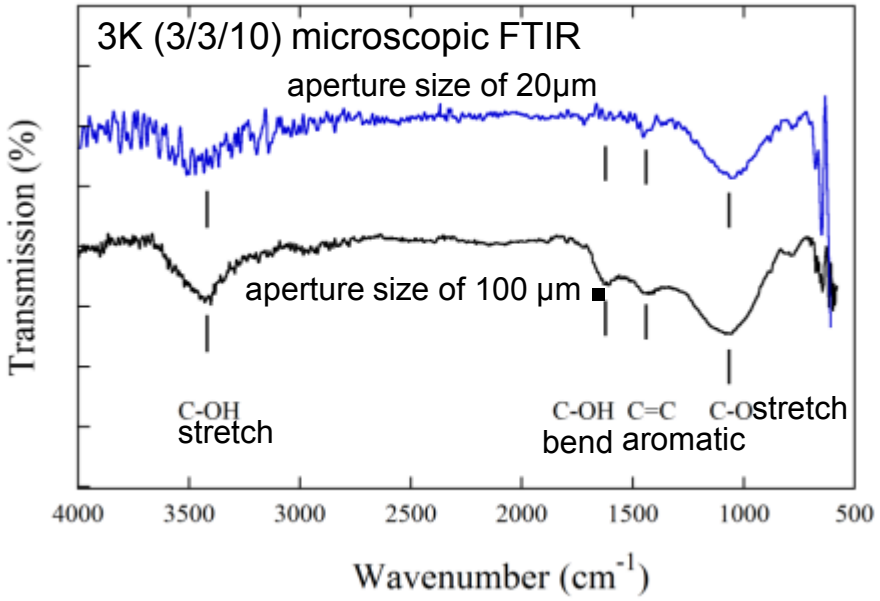
Proposed hexagonal structure that approximately achieves proper binding to atomic percent ratios.



- XPS results consistent with boron incorporated into lattice
- Room to improve remaining ~50% of boron

Technical Accomplishments

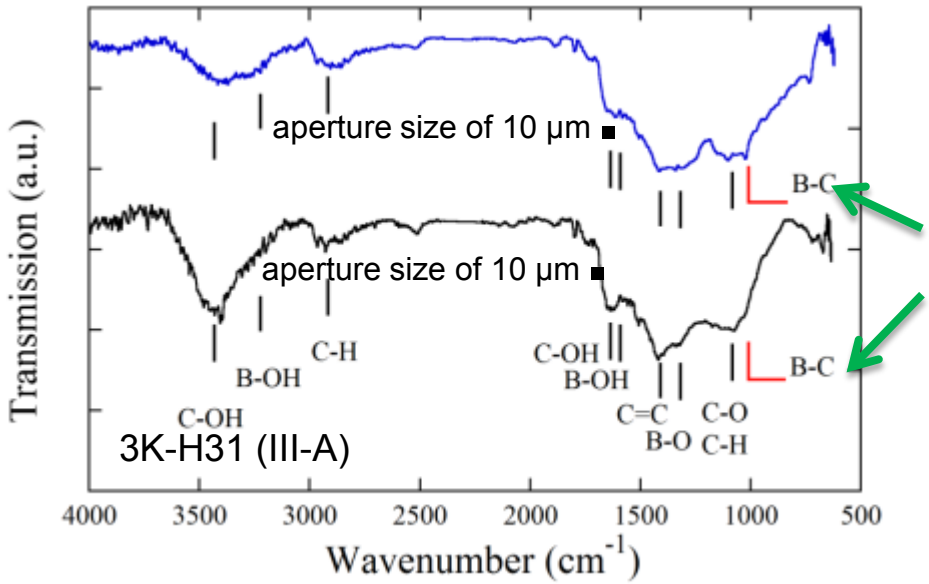
Fourier Transform Infrared Spectroscopy

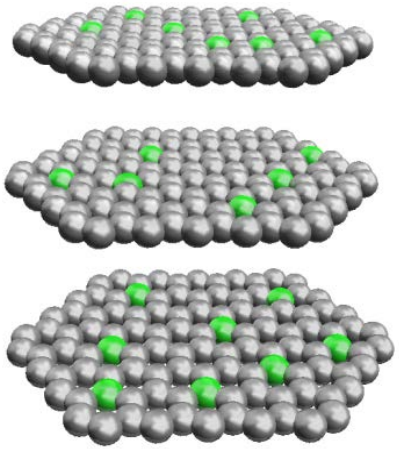


- FTIR was used in transmission mode to identify the nature of the boron bonds in boron doped activated carbon.

- **FTIR observation of line at 1022 cm^{-1} characteristic of B-C bonds** (A. P. Cote, *et al.*, "*Science,*)

- First time that the existence of B-C bonds in boron-doped carbons (vapor deposition) has been observed

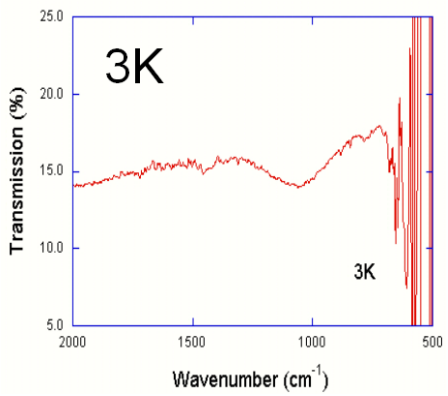


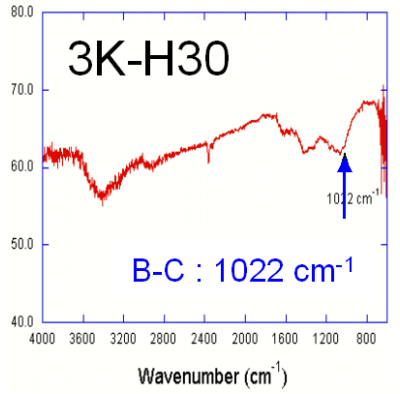


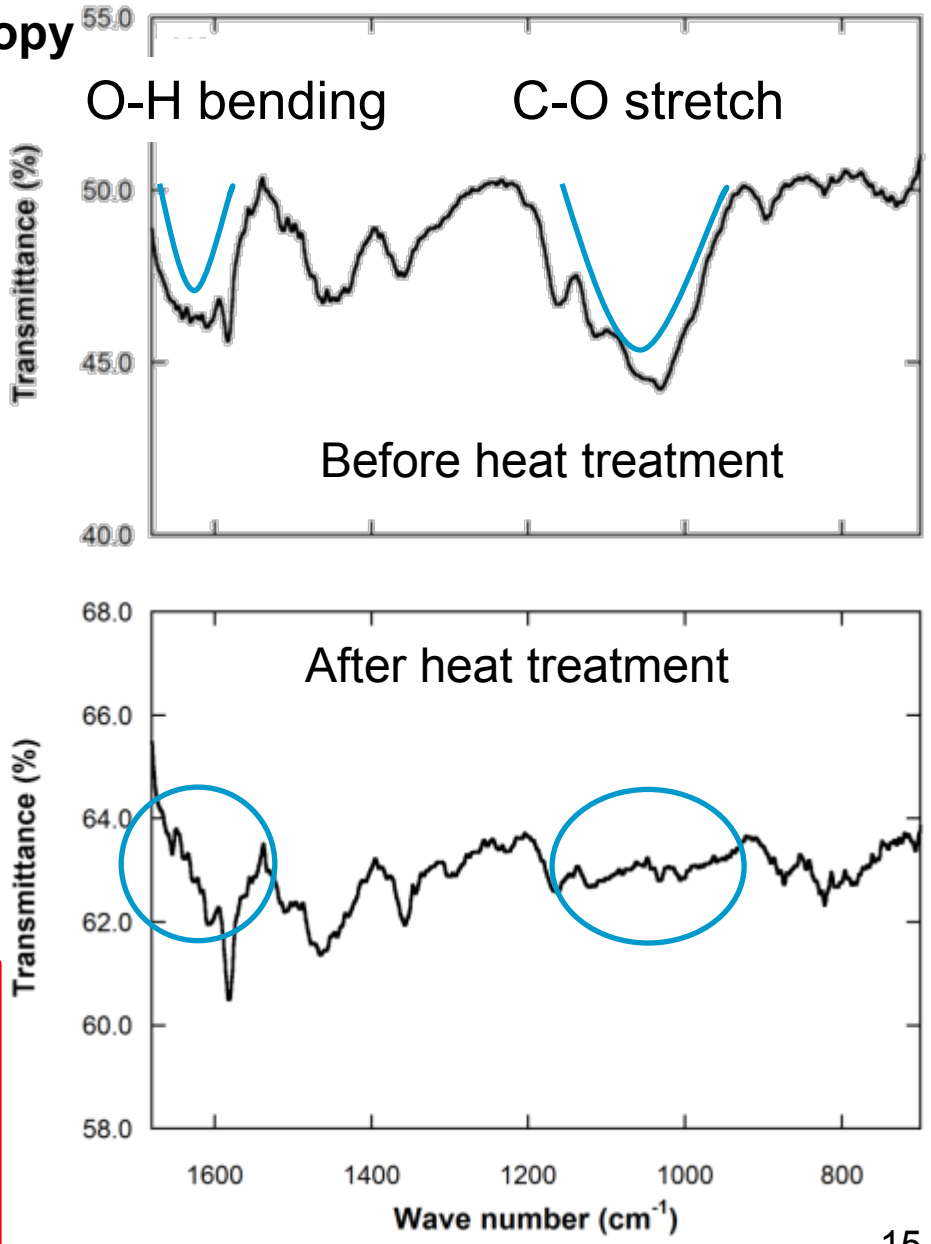
Technical Accomplishments

Fourier Transform Infrared Spectroscopy

FTIR (2011) Consistent with XPS (2012)



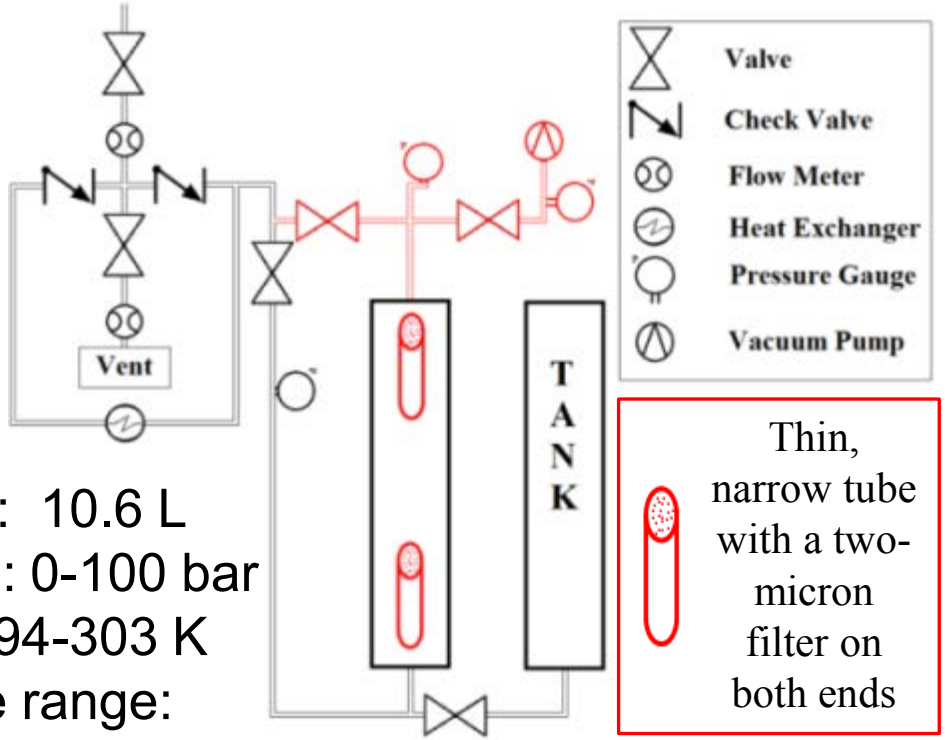




- Sample post-treatment successful in removing surface oxidation as evidenced by elimination of O-H bending and C-O stretch modes at ~1650 cm^{-1} & ~1050 cm^{-1}, respectively

Technical Accomplishments

10-liter Hydrogen Sorption Instrument

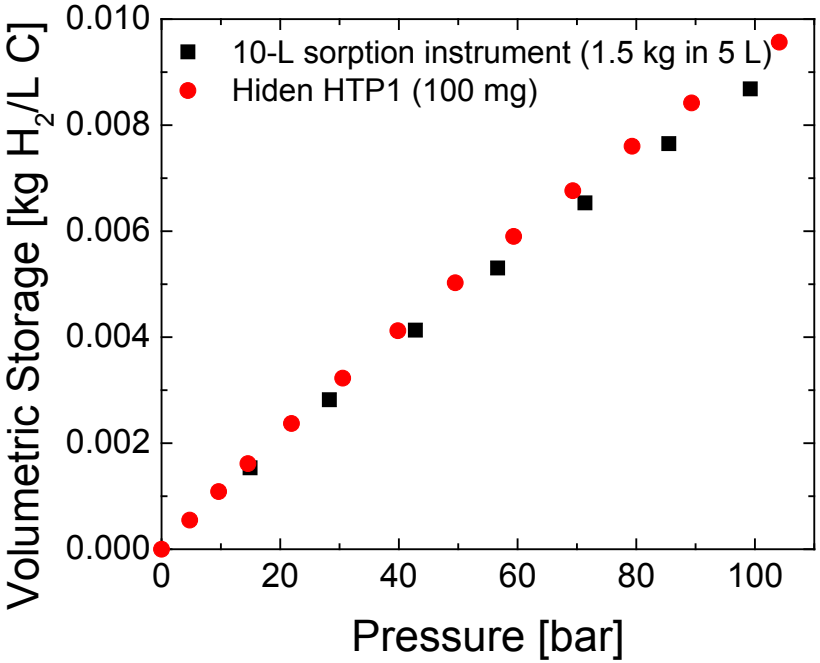


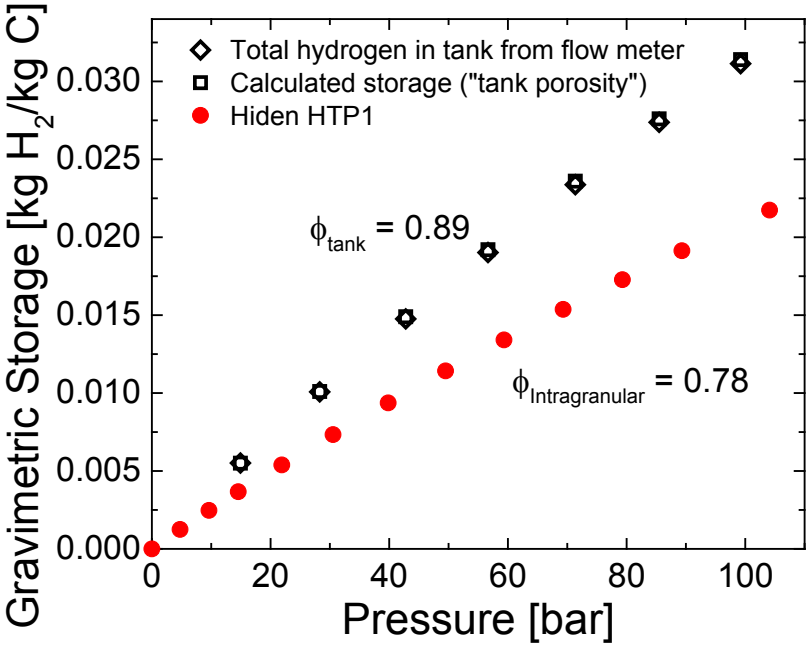
Capacity: 10.6 L
Pressure: 0-100 bar
Temp.: 194-303 K
Flow rate range:
(0-400 Ln/min H_2)

- 10-liter system capable of non-equilibrium measurements (pressure temperature, flow rate)
- Gives information about heat management and sample/tank kinetics

Technical Accomplishments

10-liter Hydrogen Sorption Instrument





$$V_{ST} \equiv G_{ex}\left(1-\phi\right)\rho_{skel} + \phi\rho_{gas}$$

$$G_{ST} = \frac{V_{ST}}{\left(1-\phi\right)\rho_{skel}}$$

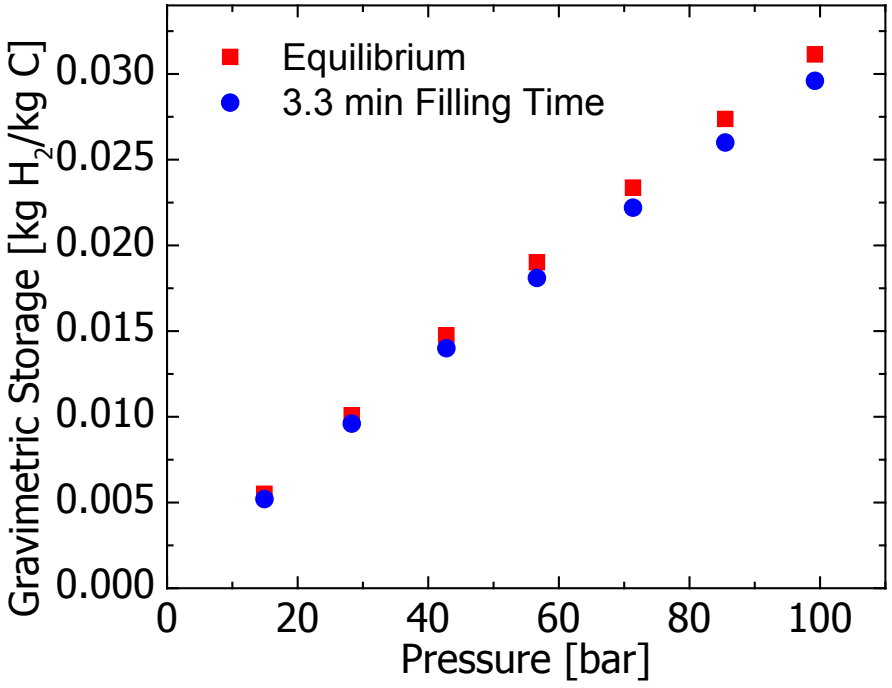
$$G_{ST} = G_{ex} + \frac{\rho_{H_2}\phi}{\left(1-\phi\right)\rho_{skel}}$$

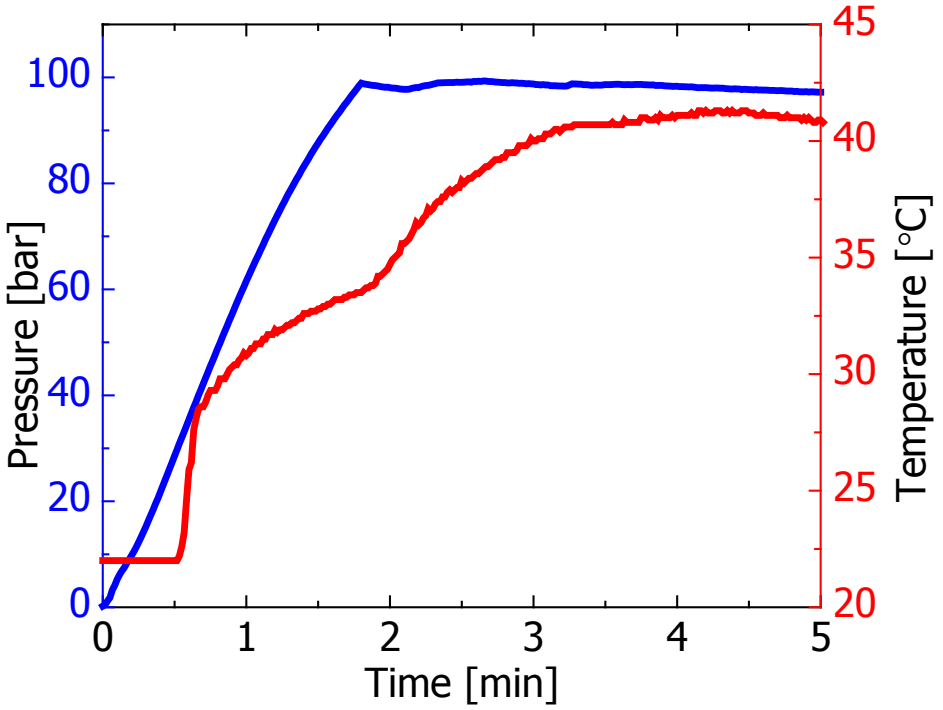
$$\phi_{intragranular} = \frac{V_{pore}}{V_{pore}+V_{skel}} < \phi_{tank} = 1 - \frac{V_{skel}}{V_{tank}}$$

- 10-liter system validated, including sorbent homogeneity
- Gravimetric storage (total) capacity of bulk material is higher than that of individual carbon grains because porosity is higher

Technical Accomplishments

10-liter Hydrogen Sorption Instrument

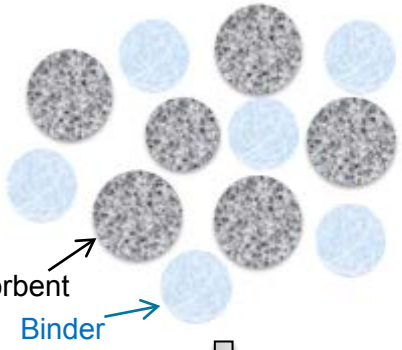




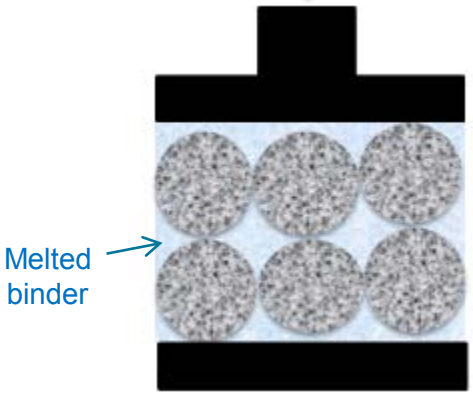
- Able to fill the tank to 95% capacity in 3.3 minutes, 303 K; no heat exchanger
- Gravimetric storage capacity will increase 5% with improved outgassing procedure

Technical Accomplishments

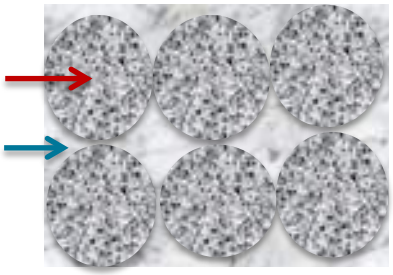
Mixing procedure



Compaction



Pyrolysis

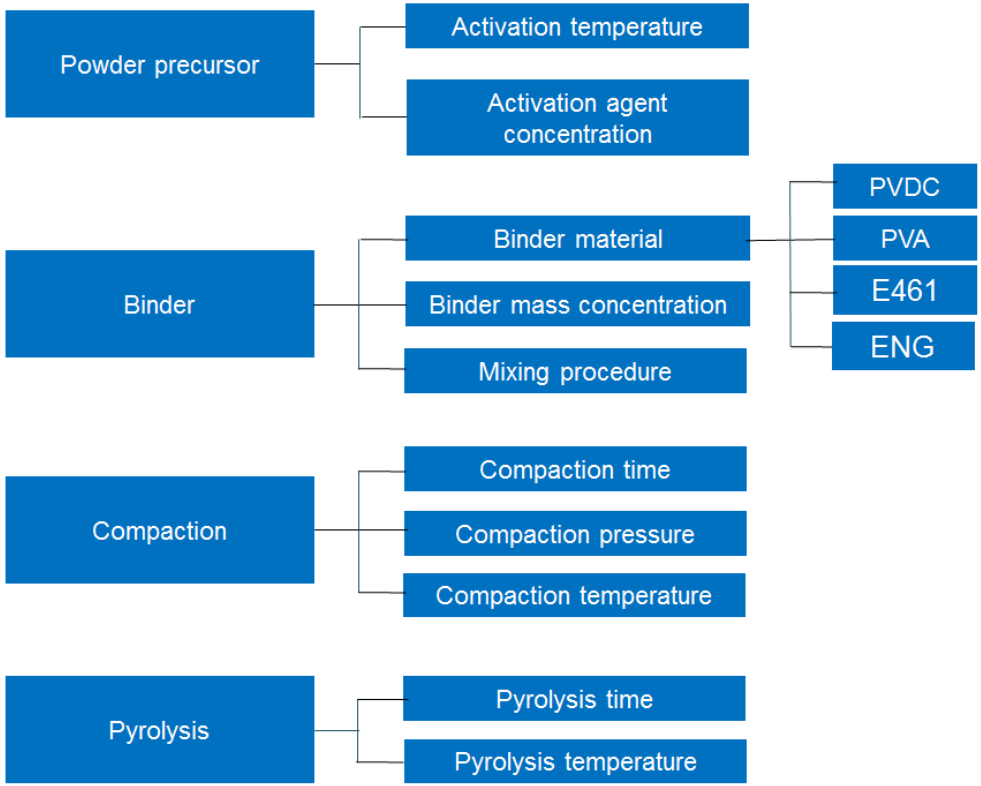


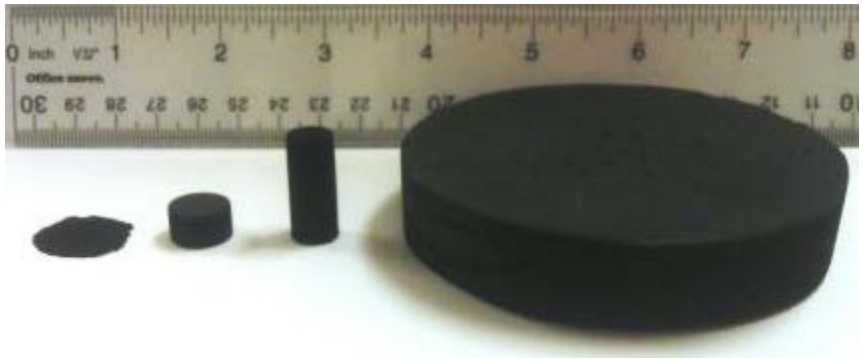
Final monolith composition:

80-85 % AC adsorbent: 2600 m^2/g

15-20 % carbon from binder: 700 m^2/g

Multi-variable optimization

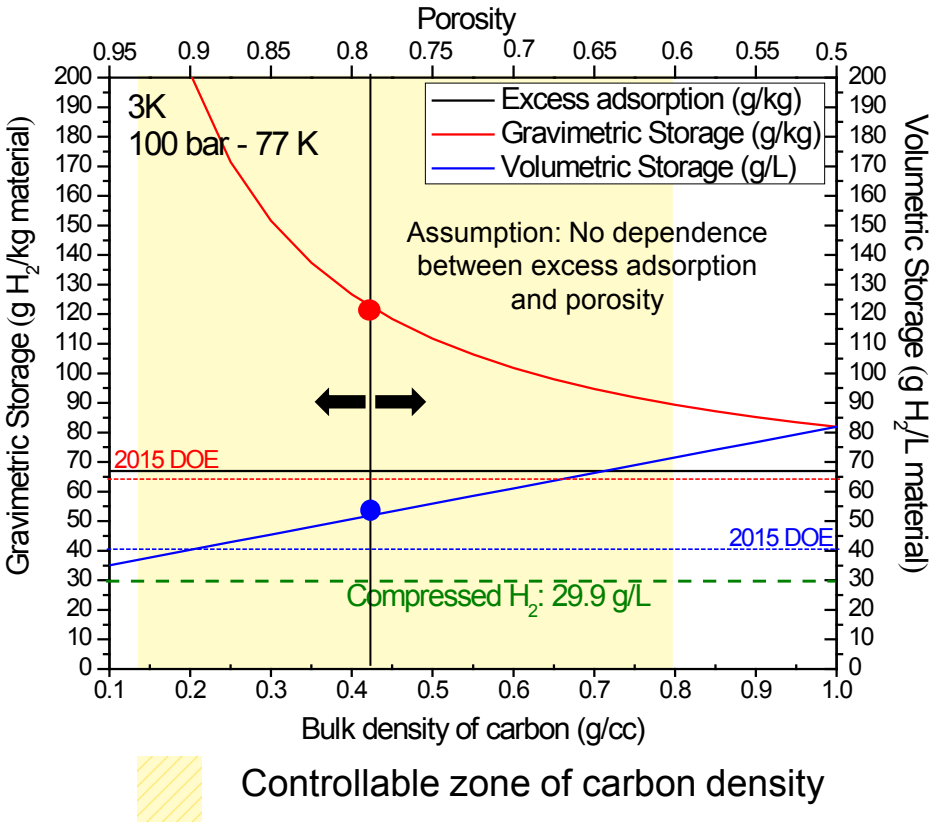


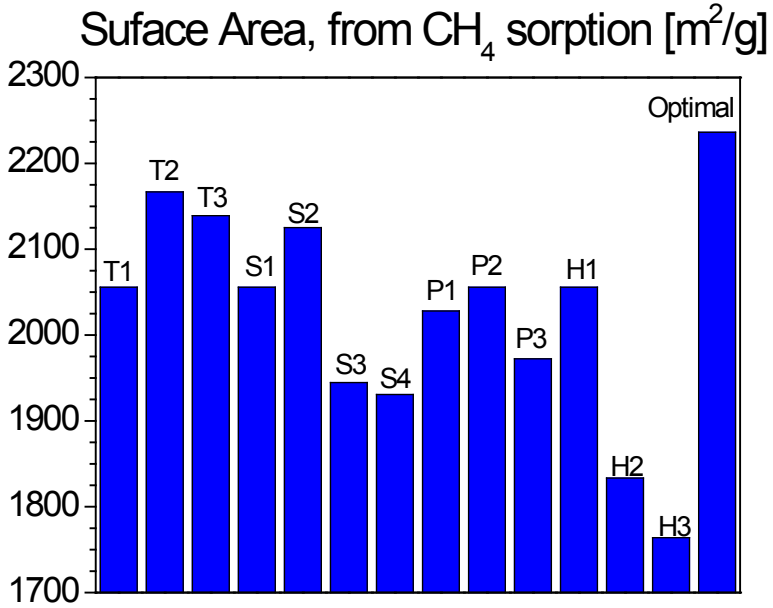


Technical Accomplishments

Optimization of Carbon Monoliths

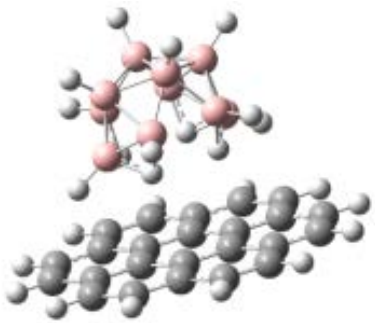
- Optimal gravimetric monolith: high surface area and high density
- Optimal volumetric monolith: high surface area and low density

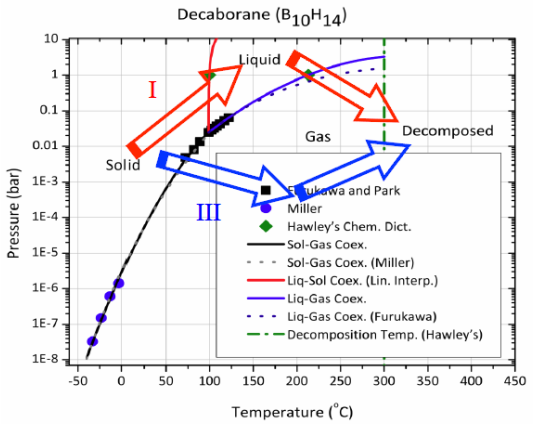


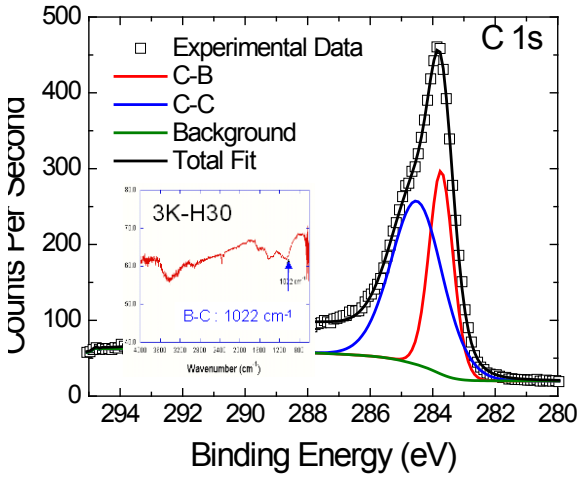


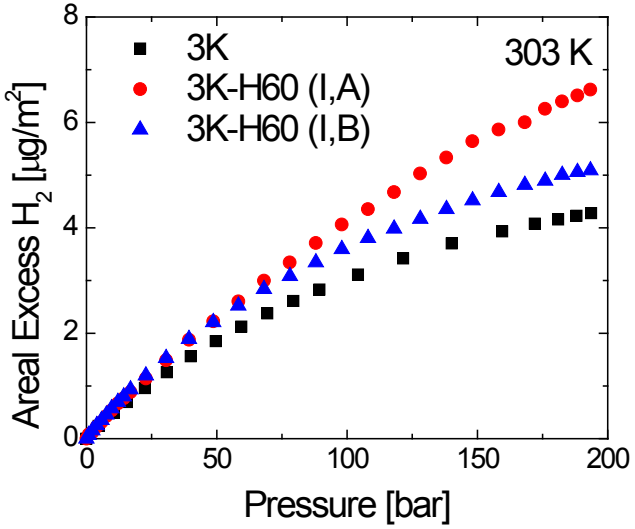
- Surface area optimized for various synthesis parameters
  - T = Compaction temperature
  - S = Binder:carbon ratio
  - P = Carbon precursor
  - H = Pyrolysis temperature
- Optimal monolith will be boron-doped & tested for hydrogen uptake

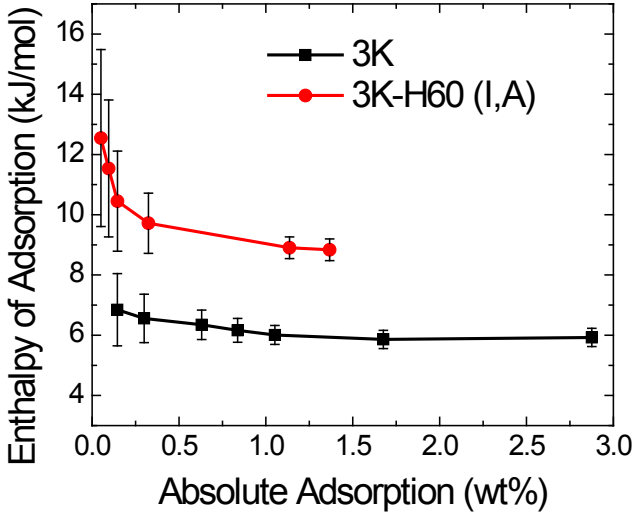
Technical Achievements (Summary)



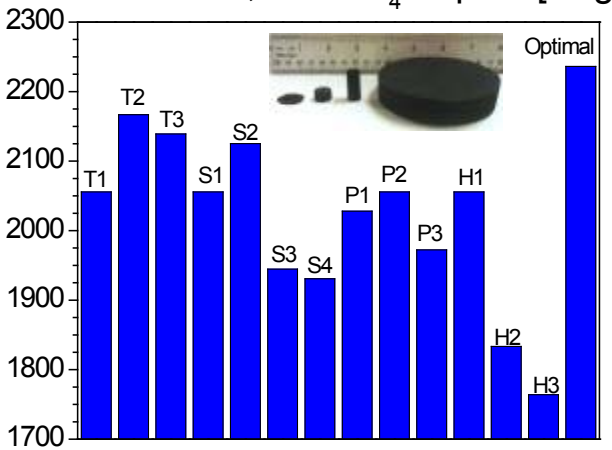








Suface Area, from CH_4 sorption [m^2/g]



- B can be incorporated into high-surface area nanoporous carbon
- Raises the binding energy and enhances excess adsorption
- Precursor monoliths optimized for surface area and await doping

Collaborations

- **Midwest Research Institute** (Subcontractor): design & construction of instrument for large-scale, automated B-doping
- **NREL** (Federal): L. Simpson, P. Parilla, K. O'Neill— Validation of H_2 uptake
- **Advanced Photon Source/ANL** (Federal): J. Ilavsky—Ultra-small-angle x-ray scattering (GUP-10069, GUP-20661)
- **NIST** (Federal): Y. Liu, G. Brown, J. Burress—small-angle neutron scattering with in-situ, adsorbed H_2
- **U. Montpellier II** & **U. Marseille**, France (Academic): L. Firlej & B. Kuchta—GCMC simulations
- **Wroclaw U. Technology**, Poland (Academic): S. Roszak—adsorption potentials for H_2 sorption on B-doped materials from ab initio quantum-chemical computations
- **ORNL** (Federal): M. Stone, R. Olsen—incoherent inelastic neutron scattering with in-situ, adsorbed H_2
- **U. Provence**, France (Academic): P. Llewellyn—microcalorimetric determination of isosteric heat of adsorption
- **U. Missouri** (Academic): M. Greenlief—XPS analysis

Future Work: Plans for 2012/13

- Characterize granular materials & demonstrate storage performance
  - Study boron-carbon bonds with micro-Raman spectroscopy & solid-state NMR
  - In-situ Raman spectroscopy of B-C bonds & mass spectroscopy of volatile reaction products during decaborane decomposition & annealing
  - Investigate advantages of multi-step doping over single step doping
  - Investigate new boron-doping methods: (i) high-temperature dissolution of boron into high-surface-area carbon; (ii) boron-carbide-derived high-surface-area materials
- Manufacture and test monolithic materials
  - Manufacture boron-doped monoliths
  - Test performance of monoliths (3.5″diameter) in 10-liter hydrogen tank during charging/discharging (temperature/pressure as a function of time; thermal management)

Project Summary, 2011-12

- Manufactured B-substituted carbon under O_2-free conditions by thermolysis of $B_{10}H_{14}$, with B:C = 7-10 wt%, without compromising high surface areas (≥ 2000 m^2/g)
- Demonstrated that B:C = 8.6 wt% raises areal excess adsorption at 303 K & 200 bar by 30% relative to undoped material, indicates increase in average binding energy, not solely highest binding energy
- Demonstrated that B:C = 8.6 wt% (annealed at 1000 C) raises areal excess adsorption at 80 K & 200 bar by 20% relative to undoped material
- Demonstrated that B-doped carbon has a significantly higher isosteric heat of adsorption (10-12 kJ/mol) vs. undoped material (5-6 kJ/mol)
- Established existence of B-C bonds in B-doped carbons, made from $B_{10}H_{14}$, using FTIR and XPS
- Understood the energetics and mechanisms of boron deposition and doping of carbon using $B_{10}H_{14}$
- Put into operation a large-scale H_2 sorption tank for non-equilibrium flow and thermal management measurements