Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Overview

Timeline

- Project start date: September 1, 2008
- Project end date: January 31, 2013
- Percent complete: 60%

Barriers

Barriers addressed:

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

Budget

- **Total project funding**:
  - DOE share: $1,899K
  - Contractor share: $514K
- **Funding for FY 2010**
  - DOE share: $350K
  - Contractor share: $227K
- **Funding for FY 2011**
  - DOE share: $314K (est)
  - Contractor share: $152K (est)

Partners

Interactions/collaborations:

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

Objectives & Relevance

Overall

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

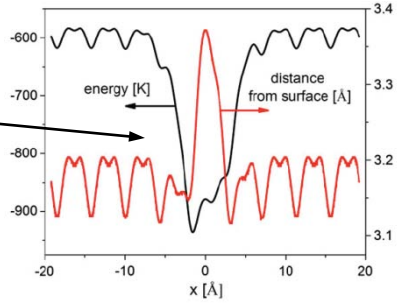
1) Determine pore-space architecture, nature of functionalized sites, H_2 sorption isotherms (1-200 bar), isosteric heats, and kinetics, at 77-300 K
2) Establish effectiveness of boron functionalization by deposition and pyrolysis of (i) decaborane ($B_{10}H_{14}$) and (ii) BCl_3 (May/2010-March/2011)
3) Establish B-C bonds in B-functionalized materials (May/2010-March/2011)
4) Establish enhanced adsorption of H_2 on B-functionalized carbon (May/2010-March/2011)
5) Use inelastic neutron scattering to probe sub-nm pores (May/2010-March/2011)
6) Validate isosteric heats obtained from adsorption isotherms by direct microcalorimetry (May/2010-March/2011)
7) Develop computational predictions of the effect of graphene edges on H_2 adsorption (May/2010-March/2011)

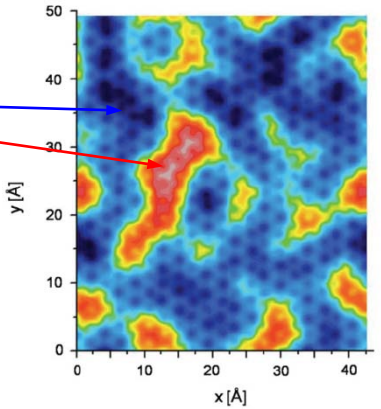
- Optimize pore architecture and composition

1) Establish optimal precursors for H_2 storage as function of KOH:C ratio and activation temperature (May/2010-March/2011)
2) Compare B-functionalized carbons produced by different synthetic methods
3) Fabricate monoliths of optimized B-functionalized carbons; determine storage capacities and charge/discharge kinetics under conditions comparable to an on-board H_2 tank

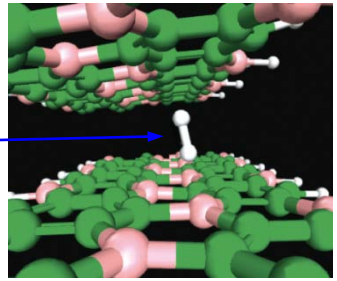
Approach—I

- Raise binding energy of H_2 on carbon by functionalization of surface with B/Li/…
  - 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; computations Firlej et al., 2009; Kuchta et al., 2010)
  - Increase in binding energy extends far beyond (~ 0.7 nm) immediate neighborhood of B-atom
  - Computed H_2 ads. isotherms (GCMC) on B:C = 10 wt% predict (Firlej et al., 2009; Kuchta et al., 2010): H_2:adsorbent = 5 wt% at room temp. and 100 bar, H_2:adsorbent = 12 wt% at liq. N_2 temp. and 100 bar





- U. Missouri: (1) Produce high-surface-area carbon (~ 3000 m^2/g), (2) Dope surface with B (> 2000 m^2/g)
  Other groups: (1) Pyrolyze C-B copolymers or synthesize B-substituted carbon scaffolds bottom-up; (2) Maximize surface area (~ 900 m^2g)
  - Reach all surface by using volatile boron carrier
  - Deposit boron by physical vapor deposition & thermolysis of $B_{10}H_{14}$
  - Deposit boron by chemical vapor deposition of BCl_3 (~ 900 °C); BCl_3 reactant for synthesis of BC_3, a candidate for H_2 intercalation (Cooper et al., 2009, 2010)
  - Incorporate B into carbon lattice by thermal annealing



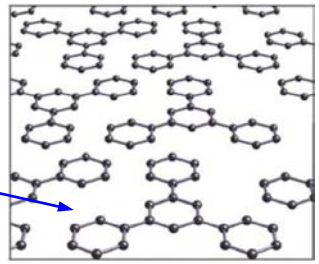
- Create nanopores (closely spaced stacks of graphene sheets)
  In narrow pores (<1 nm), adsorption potentials overlap and create deep energy wells, with binding energy up to 2 times of that in wide pores:
  - Binding energy in 0.7-nm boron-free pore: ~ 9 kJ/mol
  - Binding energy in 0.7-nm B-doped pore: ~ 18-27 kJ/mol

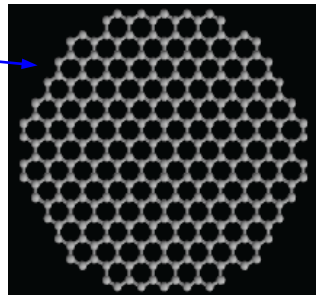
Approach—II

- Increase surface area of carbon beyond 3000 m^2/g (large single graphene sheet)
  - Use B-substituted carbon to create additional surface area by boron neutron capture (BNC); fission into Li and alpha particle,

    $^{10}B + {}^{1}n \rightarrow [^{11}B] \rightarrow {}^{7}Li + {}^{4}He + \gamma + 2.4$ MeV

    (U. Missouri Research Reactor); and etching of fission tracks
    Physical realization of Chae et al. (2004): "excision of 6-membered rings"
    For BNC: optimum track width ~ 1 nm
    For BNC: max. surf. area ~ 6000 m^2/g
  - Chemical realization of "excision of 6-membered rings" by KOH activation with large KOH:C ratio: small graphene sheets with large ratio of edge sites to in-plane sites





- Simulate H_2 adsorption (GCMC) on non-traditional surface geometries (edge sites, pore walls punctured by tranverse channels, …)
  - Objective 1: Extract pore widths and binding energies from exp. H_2 isotherms
  - Objective 2: Identify conditions under which multilayer adsorption is significant
  - Objective 3: Identify contributions to H_2 adsorption from in-plane sites and edge sites
  - Objective 4: Determine film volume for correct determination of isosteric heat from Clausius-Clapeyron equation (Olsen et al, 2011)
  - Objective 5: Determine density of saturated film, $\rho_{film}(T)$, as function of temp. and surface geometry; compare with exp. densities; find surface geometries/chemistries that give high $\rho_{film}(T)$ and E_B

- Manufacture monoliths of B-doped carbon for conformable, lightweight tank
  - Minimizes wide pores; minimizes tank volume
  - Low pressure, 100 bar, enables conformable tank design
  - High binding energy, 15 kJ/mol, enables storage at room temp.

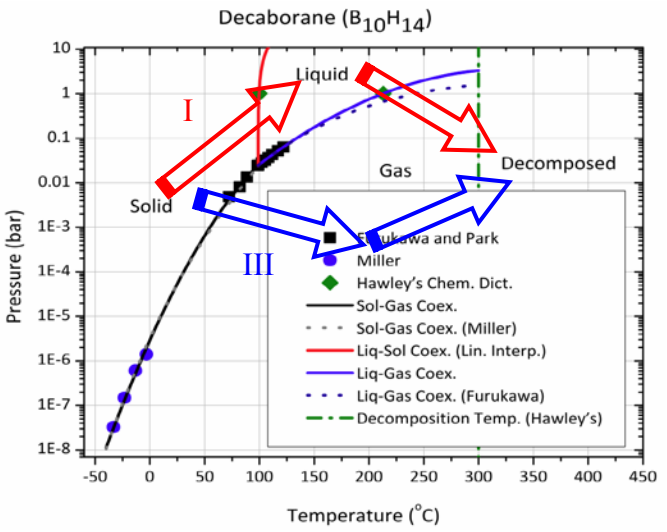
Approach—III: Tasks (revised)

Task	Progress Notes	% Comp
1. Fabricate functionalized carbons		
Fabricate B-doped materials by vapor deposition & thermolysis of decaborane	Production *in O_2-free environment* achieved. Samples characterized. *Increase in excess adsorption observed*. Pending: chemical pathways and optimization	70%
Fabricate B-doped materials by vapor deposition & thermolysis of BCl_3	Production with B:C = 2 wt% achieved. Pending: sample characterization; chemical pathways; optimization	30%
Creation of fission tracks by boron neutron capture (BNC)	Fission tracks created at U. Missouri Research Reactor	80%
Creation of new surface area by etching of fission tracks	Etching of fission tracks performed with hydrogen peroxide. Gave no increase in surface area. Pending: high-T steam oxidation (on hold)	70%
Manufacturing of monoliths	Boron-free monoliths manufactured and tested. *Gravim. storage capacity comparable to best powders. Volum. capacity better than powders*	50%
2. Fabricate hybrid materials	No longer under consideration (HSCoE assessment of spillover effect not conclusive)	0%
3. Characterize and optimize materials/H_2 storage performance		
Map pore space by SAXS, N_2 adsorption, H_2 isotherms, SEM/TEM,	SAXS methodology complete, new sample characterization via SAXS now standard (shape, width, length, wall thickness, porosity), applied to numerous samples. N_2 BET and PSD routine. Incoherent inelastic neutron scattering theory and experiments. *FTIR observation of B-C bonds*	75%
Predict H_2 isotherms in pure-C and B-substituted materials, and compare with experimental isotherms.	GCMC and MD simulations of H_2 isotherms in good agreement with experiments. QC computations of H_2 binding energies for B-doped C. *Significance of edge adsorption determined*	75%
Measure H_2 binding energies from adsorption isotherms and microcalorimetry	*Highest excess adsorption for B-doped sample* produced under O_2-free conditions. Developed method for isosteric heat determination at high and low coverage. *Validated by microcalorimetric measurements*	70%
Compare different methods of B functionalization	*Best result (highest excess adsorption) achieved on sample B-doped with decaborane under O_2-free conditions*	70%
Optimize gravimetric & volumetric storage capacities	Analyzed performance of compacted powders under mechanical pressure vs. monoliths. *Compacted powders not competitive*	80%
Design test vessel for monoliths	Not started, as directed by DOE Program Management. *Test vessel for operation at room temp. & O_2-conditions exists from another project*	100%
4. Characterize and optimize monoliths		
Construct test vessel for monoliths	Not started, as directed by DOE Program Management. *Test vessel for operation at room temp. & O_2-conditions exists from another project*	100%
Instrument for B-doping of monoliths with decaborane	Design complete. Pending: construction and deployment	30%
Validate and optimize B-doped monoliths	Not started, as directed by DOE Program Management	0%

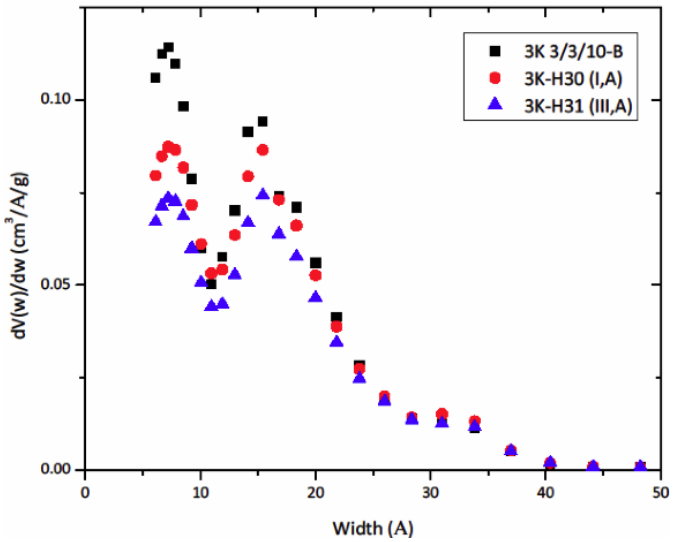
Technical Accomplishments – Summary of 2010 AMR

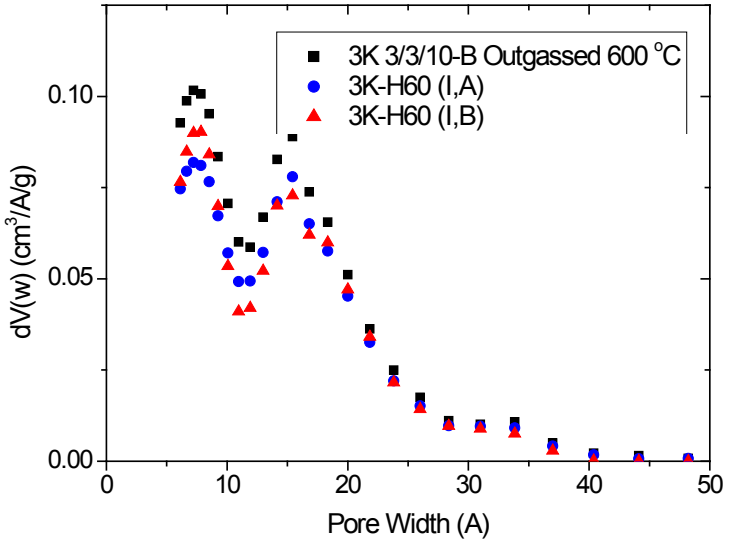
- Validation of H_2 isotherms in independent labs (MU, NREL, “Blind”): reproducibility ~ 5%
- B-doping & neutron irradiation, fission tracks
- B-doping raised average binding energy to 9-11 kJ/mol (B:C = 1.4 wt%)
- Found unexpected variations of exp. saturated-film densities and pressure at which excess adsorption has local maximum
- Theory of isosteric heats at all coverages: concluded that *absolute adsorption* must be used.
- Ab initio + GCMC results for B-substituted carbon
- Excess adsorption at 80 K and 303 K for a large “library” of samples
- Structural characterization of samples: SAXS & TEM

Technical Accomplishments 1 – $B_{10}H_{14}$-doped materials (O_2-free)



Sample	Precursor	B:C %	Σ_{N2} (m^2/g)	Φ_{N2}	Notes
3K 3/3/10-B	Self	0.0	2,700	0.77	
3K-H30 (I,A)	3K 3/3/10-B	8.4	2,300	0.75	B-H Decomp., 600 °C
3K-H31 (I,A)	3K 3/3/10-B	10.0	2,000	0.73	B-H Decomp., 600 °C
3K 3/3/10-B out-gassed @ 600 °C	Self	0.0	2,600	0.76	
3K-H60 (I,A)	3K 3/3/10-B out-gassed @ 600 °C	8.6	2,100	0.73	B-H Decomp., 600 °C
3K-H60 (I,B)	3K 3/3/10-B out-gassed @ 600 °C	6.7	2,100	0.72	B-H Decomp., 1,000 °C

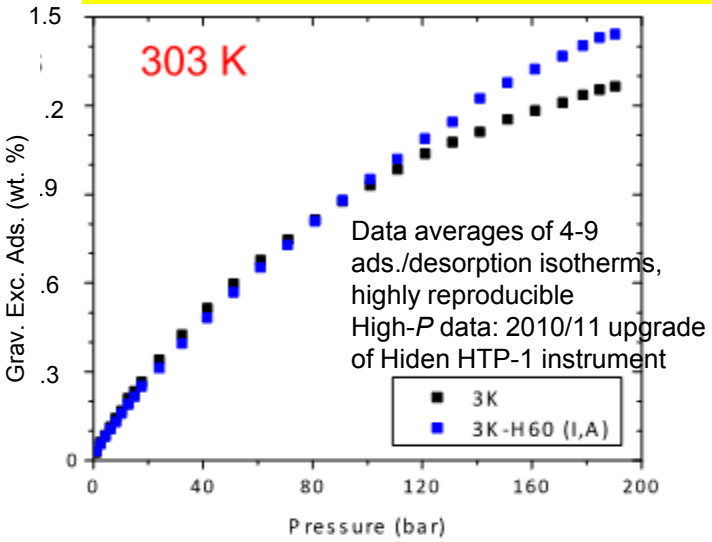


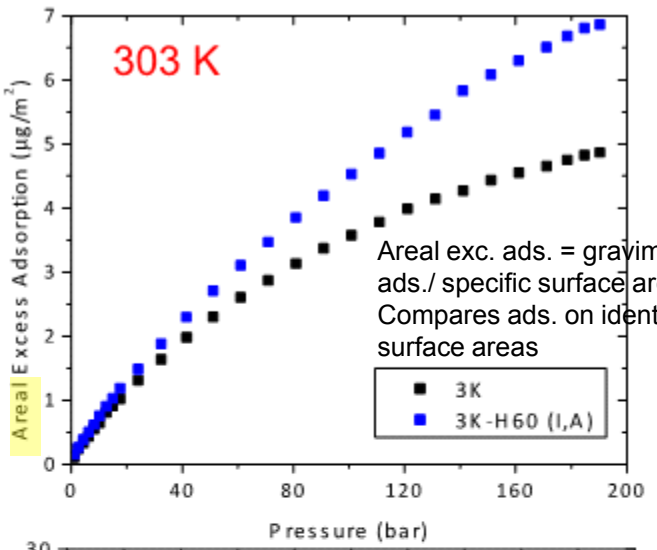


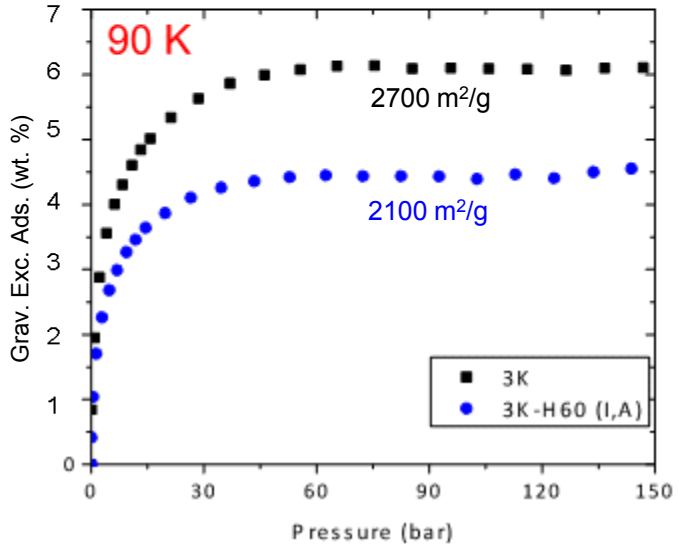
Conclusions:

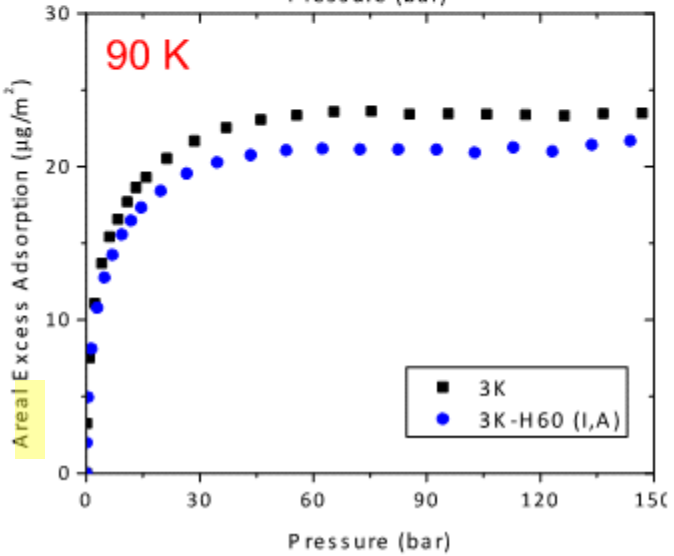
- **Achieved B:C = 10% (Method I), but at a cost of some pore blockage (surface area ~ 2000 m^2/g).**
- **For B:C = 10 wt% w/o blocking, it is necessary to apply Method III multiple times.**
- **Apparatus for automated doping with $B_{10}H_{14}$ under construction (MRI).**

Technical Accomplishments 1 – $B_{10}H_{14}$-doped materials (contd.)









Conclusions:

- **For B:C = 8.6 wt%: areal excess adsorption at 303 K & 200 bar 30% higher than on undoped material**
- **Increase in areal excess adsorption at high *T* & *P* indicates increase in *average* binding energy, not just highest binding energy (increased binding energy in large pores, consistent with liquid $B_{10}H_{14}$ doping). Increase not observed at 90 K because unblocked pores in undoped material support H_2 multilayers, not available in doped material**
- **O_2-free conditions crucial for increased ads. on B-doped sample (no increase observed with O_2; 2010 Report)**

Technical Accomplishments 2 – Optimization of Pore Geometry, Undoped Samples

- Ground corncob is soaked with phosphoric acid and charred at 480°C under nitrogen.
- The activation mechanism by potassium hydroxide is a complicated process and consists of several simultaneous/consecutive chemical reactions.

Corncob

$2KOH \rightarrow K_2O + H_2O$ $(dehydration)$

$C + H_2O \rightarrow CO + H_2$ $(water - gas\ reaction)$

$CO + H_2O \rightarrow CO_2 + H_2$ $(water - gas\ shift\ reaction)$

$CO_2 + K_2O \rightarrow K_2CO_3$ $(carbonate\ formation)$

Above 700°C

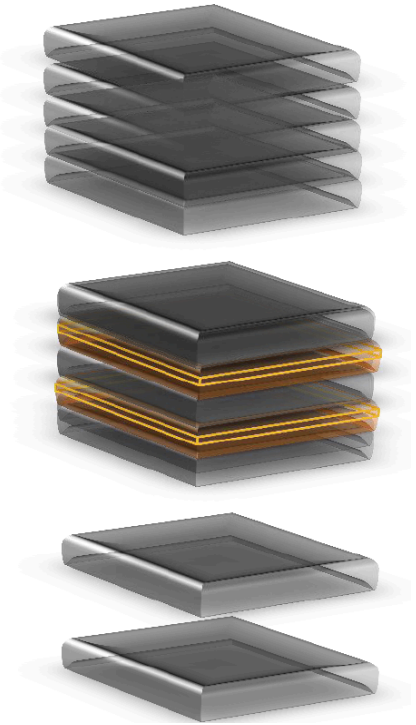
$K_2O + H_2 \rightarrow 2K + H_2O$ $(reduction\ by\ hydrogen)$

$K_2O + C \rightarrow 2K + CO$ $(reduction\ by\ carbon)$

Activation mechanism

Consumption of carbon by oxygen producing carbon monoxide and carbon dioxide

- **Penetration of metallic potassium into the graphitic lattice**
- Expansion of the lattice by the intercalated potassium
- Rapid removal of the intercalate from the carbon sheet

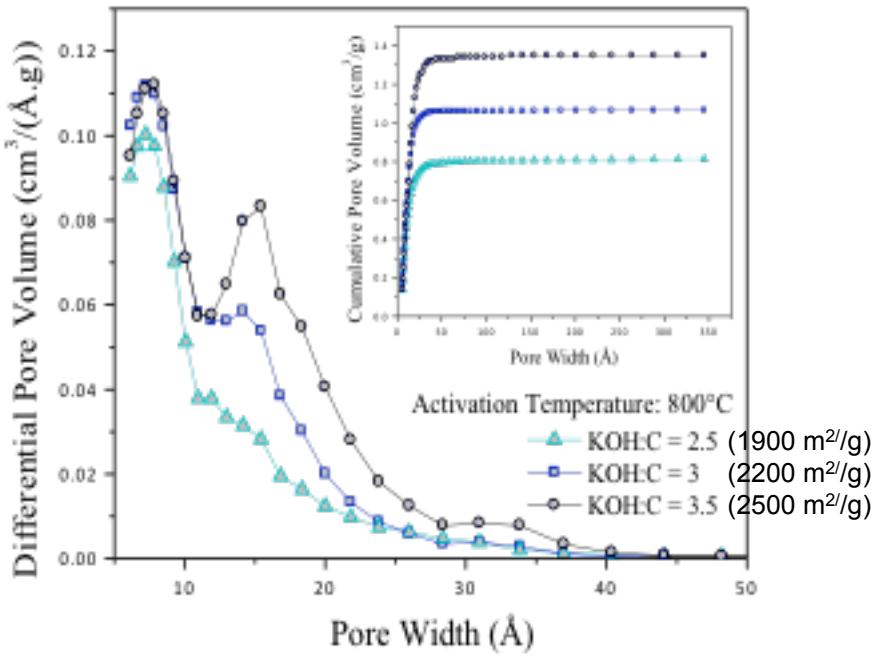


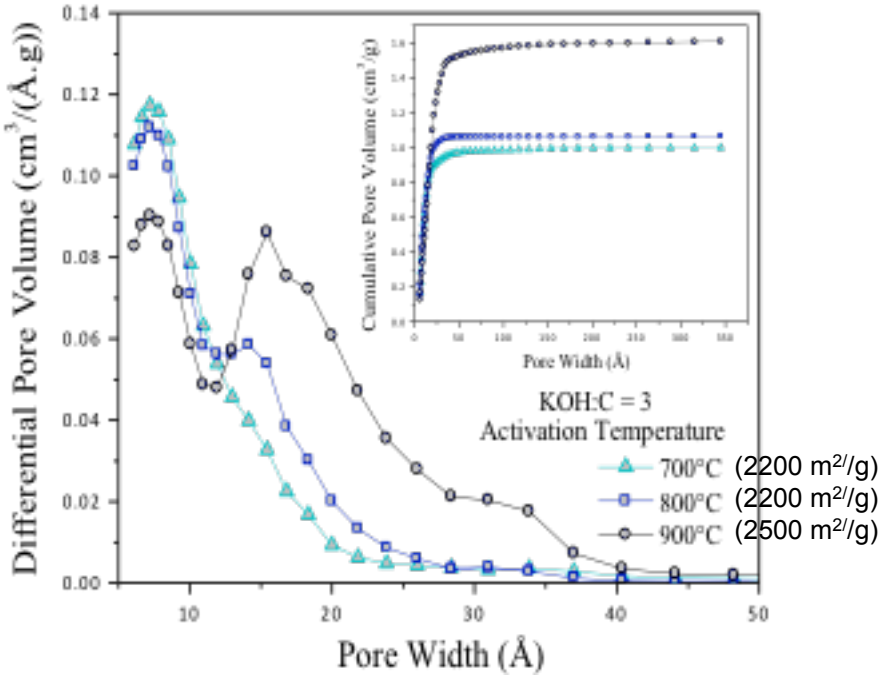
Pore structure is controlled by two fabrication parameters

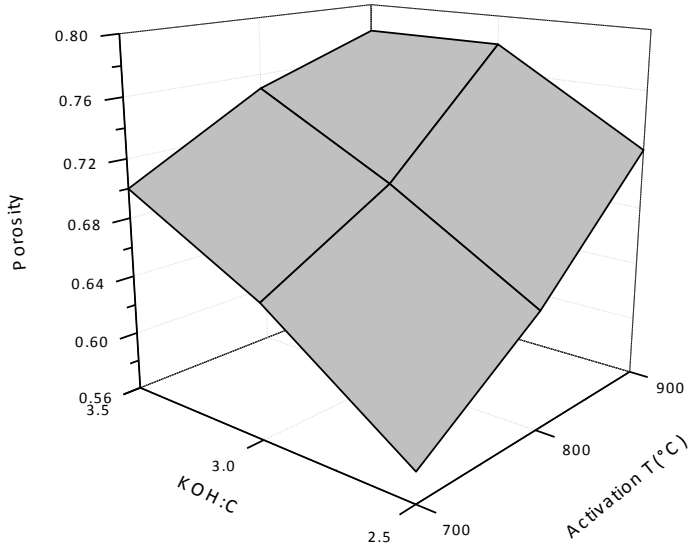
1. **Activation temperature**
2. **KOH:C weight ratio**

Technical Accomplishments 2 – Optimization of Pore Geometry, Undoped Samples (contd.)

Optimization of precursor pore geometry: activation agent concentration and activation temperature



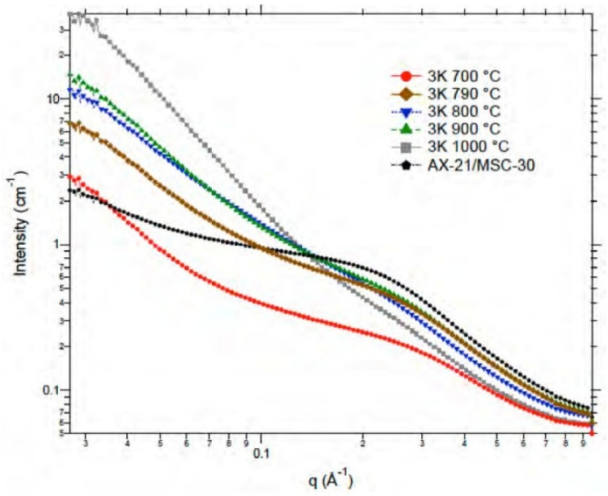




Conclusions:

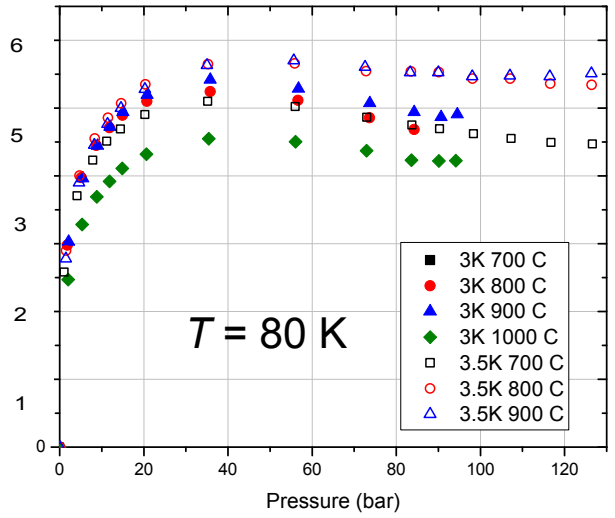
- **High KOH:C ratio and high *T* lead to larger pore volumes, larger porosity, larger surface area**
- **But narrow pores are lost at high KOH:C and *T***
- **Model for low KOH:C and *T*: Large graphene sheets, closely stacked**
- **Model for high KOH:C and *T*: Small graphene sheets, losely stacked (precursor of > 3000 m^2/g)**
- **Optimal for H_2 storage? See next pages**

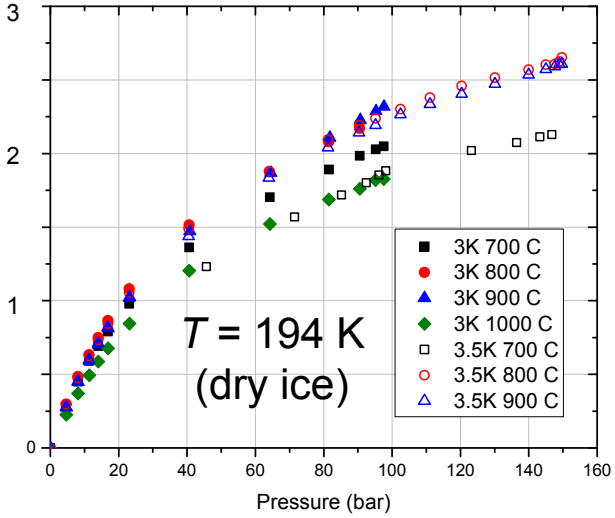
Technical Accomplishments 2 – Optimization of Pore Geometry, Undoped Samples (contd.)

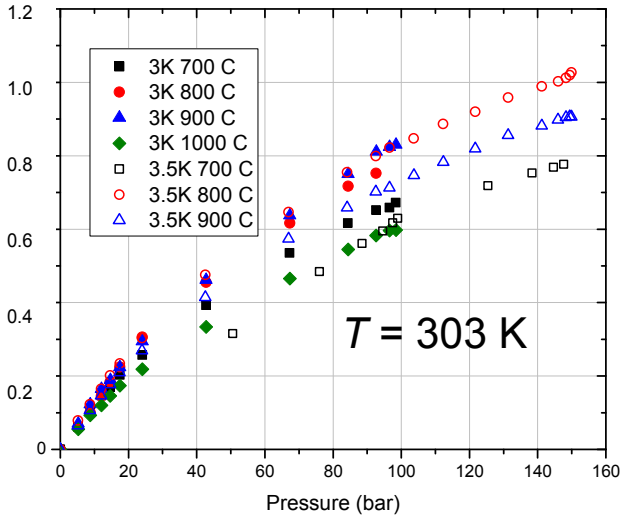


Small-angle x-ray scattering (SAXS) intensity as a function of the scattering vector, q, for samples 3K-700ºC, 3K-790ºC, 3K-900ºC, and 3K-1000ºC, and AX-21/MSC-30. Increasing temperature causes an increase of the power-law slope measured at q = 0.2 Å^{-1}. A horizontal plateau in this region of the scattering curve signals the presence of well-defined nanopores. The increase in the power-law slope indicates the destruction of this network.

Gravimetric excess adsorption (wt.%):







Conclusions:

- **Optimized gravim. excess adsorption for undoped carbons (table next page): Sample 3.5K 800 C consistently outperforms others; ideal balance between large cumulative pore volume and existence of narrow pores.**

Technical Accomplishments 2 – Optimization of Pore Geometry, Undoped Samples (contd.)

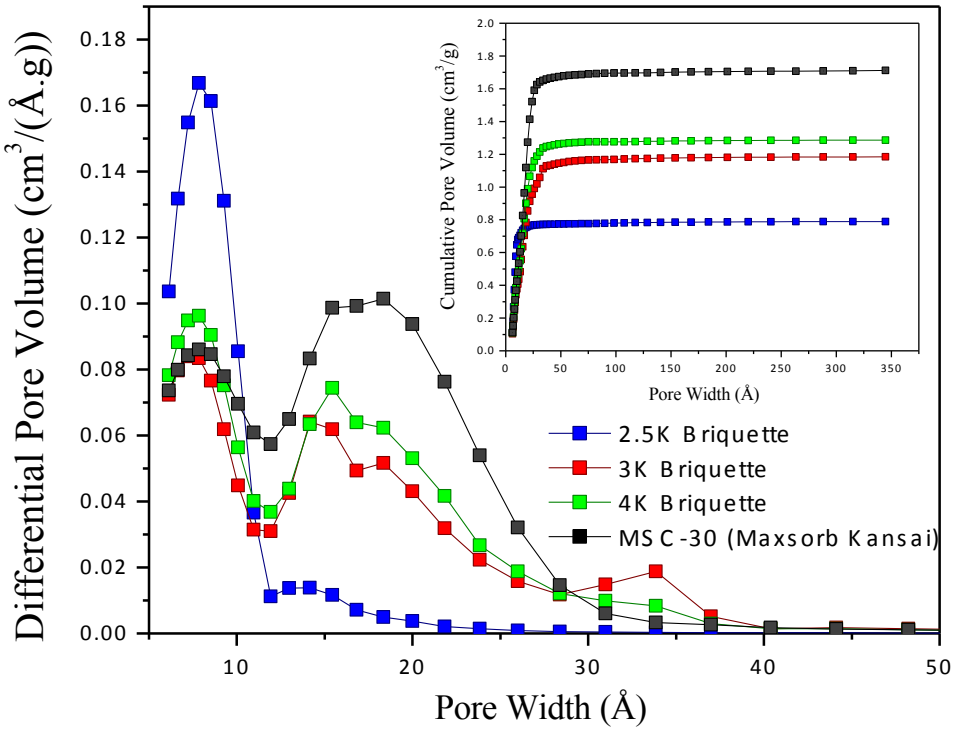
Sample	Σ_{N2} (m^2/g)	Φ_{N2}	Grav. Exc. Ads. 100 bar, 303 K (wt. %)	Grav. Exc. Ads. 100 bar, 194 K (g/kg)	Grav. Exc. Ads. 100 bar, 80 K (g/kg)
2.5K 800 °C	1900	0.69	0.53	1.62	N/A
3K 700 °C	2200	0.65	0.67	2.01	N/A
3K 800 °C	2200	0.78	0.74	2.12	4.47
3K 900 °C	2500	0.78	0.82	2.28	4.68
3K 1000 °C	2000	0.78	0.60	1.80	4.05
3.5K 700 °C	2000	0.70	0.63	1.85	4.42
3.5K 800 °C	2500	0.75	0.84	2.18	5.15
3.5K 900 °C	2500	0.78	0.70	2.14	5.18
4K 800 °C	2600	0.81	0.56	N/A	5.02
5K 790 °C	3200	0.81	0.65	N/A	4.03

Summary of undoped carbons. Gravimetric excess adsorption at 100 bar. Best performances are highlighted in yellow.

Technical Accomplishments 3 – Powders vs. Monoliths (Briquettes)

Sample	From nitrogen isotherms		Macroscopic measurements		
	Intragranular density (g/cm^3)	Intragranular porosity	Bulk density (g/cm^3)	Bulk porosity	BET surface area (m^2/g)
MSC-30	0.42	0.79	NA	NA	2600
2.5K Briquette (30% binder)	0.74	0.63	0.70	0.65	2000
3K Briquette (25% binder)	0.56	0.72	0.47	0.77	1900
4K Briquette (25% binder)	0.53	0.74	0.37	0.81	2100

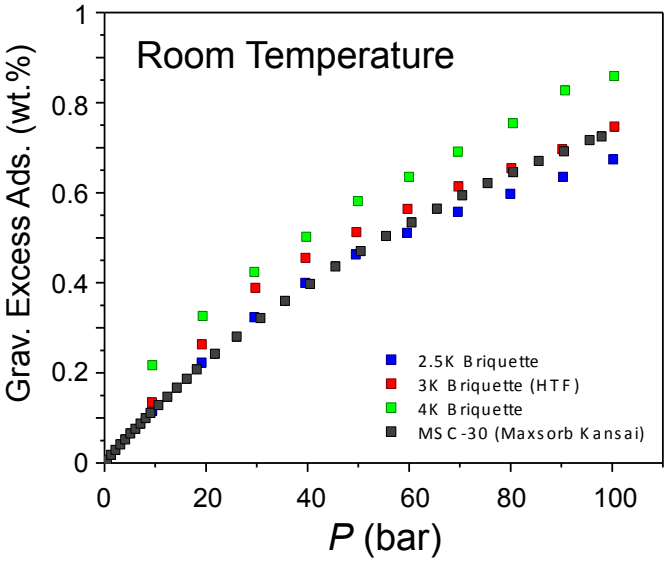
Powdered activated carbon is pressed into briquettes at 1000 bar using PVDC as a chemical binder. The volume concentration of PVDC is 25-30%.



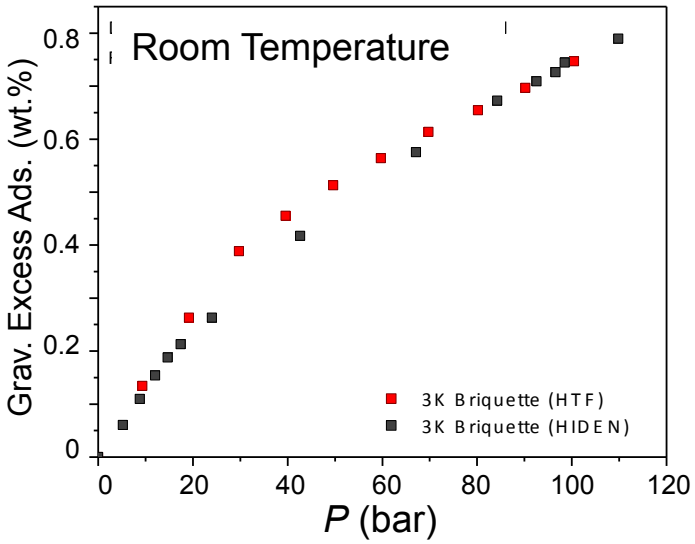
0.5-liter Hydrogen Test Fixture (HTF, Sievert apparatus, room temp.)

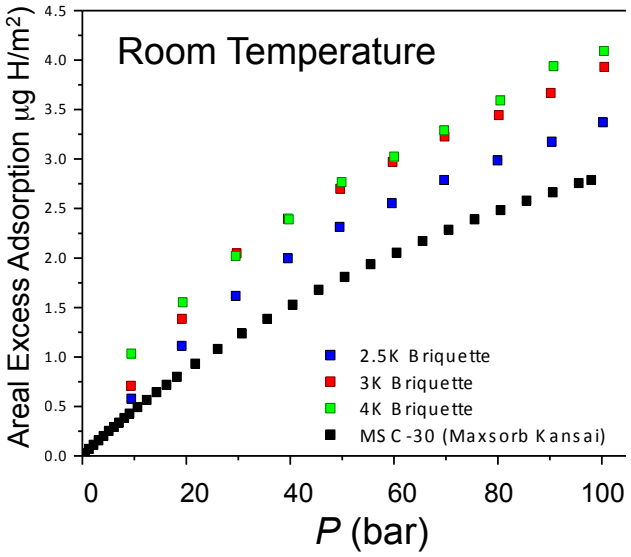
10-liter sorbent-based hydrogen tank (dry-ice temp., room temp.)

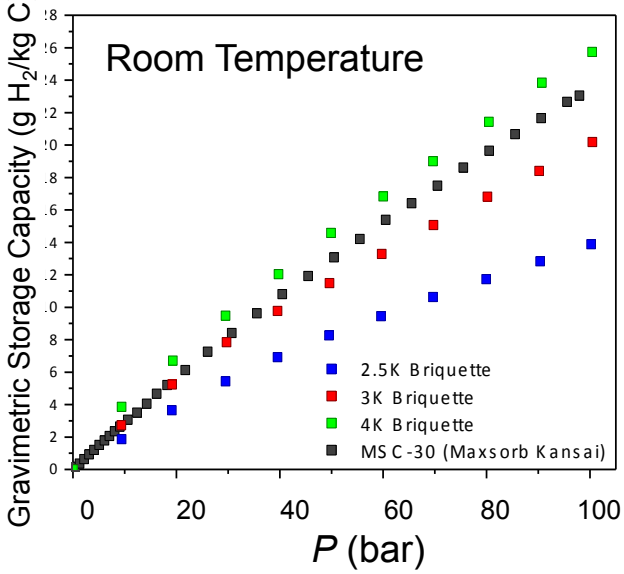
Technical Accomplishments 3 – Powders vs. Monoliths (contd.)

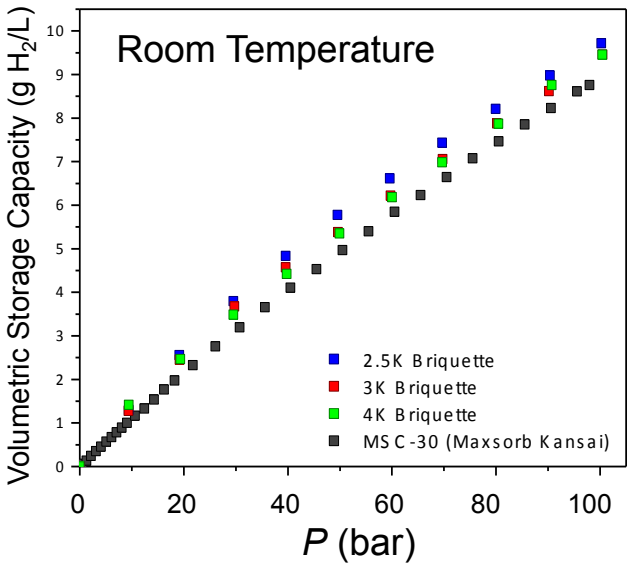


Validation between HTF and HIDEN









All briquette data measured on HTF, unless otherwise indicated

Technical Accomplishments 3 – Powders vs. Monoliths (contd.)

Sample	BET surface area (m^2/g)	Intragranular density (g/cm^3)	Intragranular porosity	Room Temp. Grav. Excess Adsorption (100 bar) (g/kg)	Room Temp. Grav. Storage Capacity (100 bar) (g/kg)	Room Temp. Vol. Storage (100 bar) (g/L)
2.5K powder	1900	0.62	0.69	5.3	13.2	8.2
3K powder	2600	0.44	0.78	9.3	21.8	9.6
4K powder	2600	0.38	0.81	5.6	20.6	7.8
MSC-30	2600	0.42	0.79	7.2	23.0	8.8
2.5K Briquette (30% binder)	2000	0.74	0.63	6.7	13.9	9.7
3K Briquette (25% binder)	1900	0.56	0.72	7.5	20.2	9.5
4K Briquette (25% binder)	2100	0.53	0.74	8.6	25.7	9.5

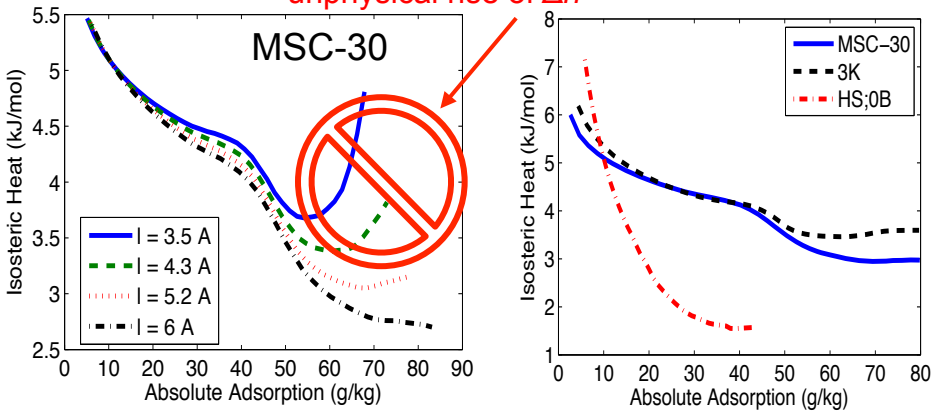
Conclusions:

- **Carbon made from PVDC improves hydrogen uptake at room temperature (HS;0B, 2010 Report). [measurements on 0.5-liter HTF validated on Hiden HTP-1 instrument]**
- **Briquettes outperform most powder samples in terms of volumetric storage capacity because low porosity gives high volumetric storage capacity. 2.5K briquette has only sub-nm pores and gives highest volumetric storage capacity, 9.7 g H_2/liter C at 300 K & 100 bar**
- **All briquettes outperform MSC-30 at room temperature in terms of *volumetric storage capacity* and *areal excess adsorption*. 4K briquette outperforms MSC-30 in terms of *gravimetric storage capacity***
- **The performance of several briquettes is explained by the pore size distribution (previous slide)**
- **Large samples, on 0.5-liter HTF, lead to less dependence on sample inhomogeneity**
- **10-liter tank: will permit studies of flow rates, thermal management, and operation at dry ice temperature (194 K)**

Technical Accomplishments 4 – Isosteric Heat Measurements

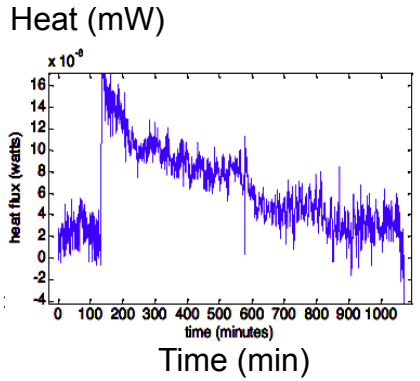
"Best methods" for determination of isosteric heats: *experimental determination of film thickness*

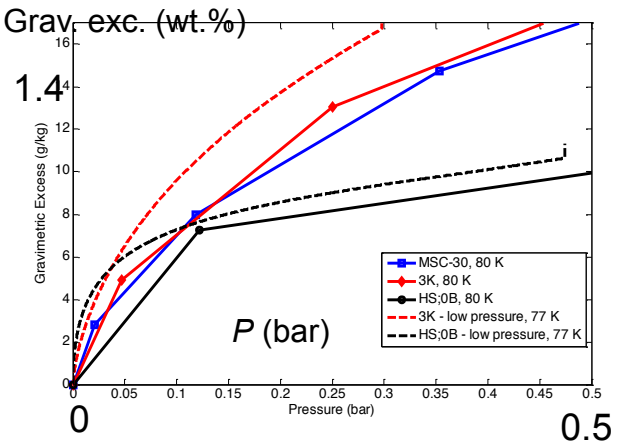
absolute adsorption: avoid unphysical rise of Δh

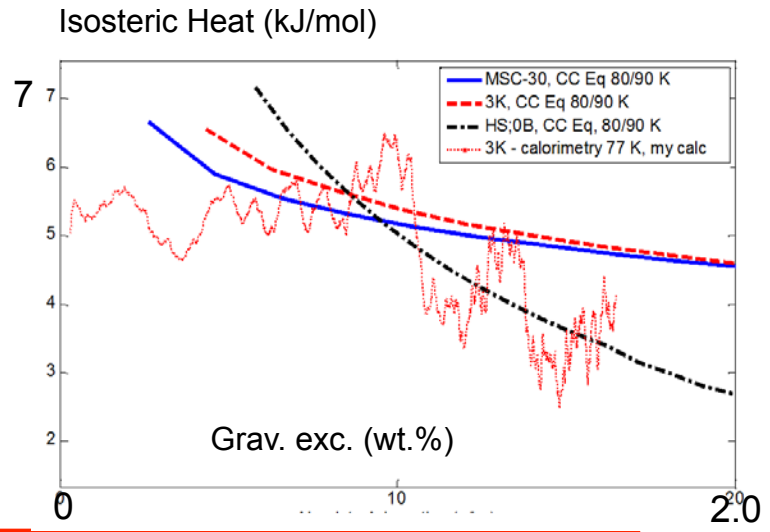


sample	type	*l* (Å)	m_e/Σ ($\mu g/m^2$)	Δh (kJ/mol)
MSC-30	AC	5.4	19.6	6.0-3.0
3K	AC	5.1	21.0	6.2-3.6
HS;0B	PVDC	5.3	52.8	7.2-1.6
Li+Wu(2009)	Zeolite NaX		29.3	4.1-?
Saha (2008)	MOF-177		33.6	4.0-0.5
Saha (2009)	MOF-5		28.1	2.6-2.1

Microcalorimetry (77 K) – collaboration with U. Marseille





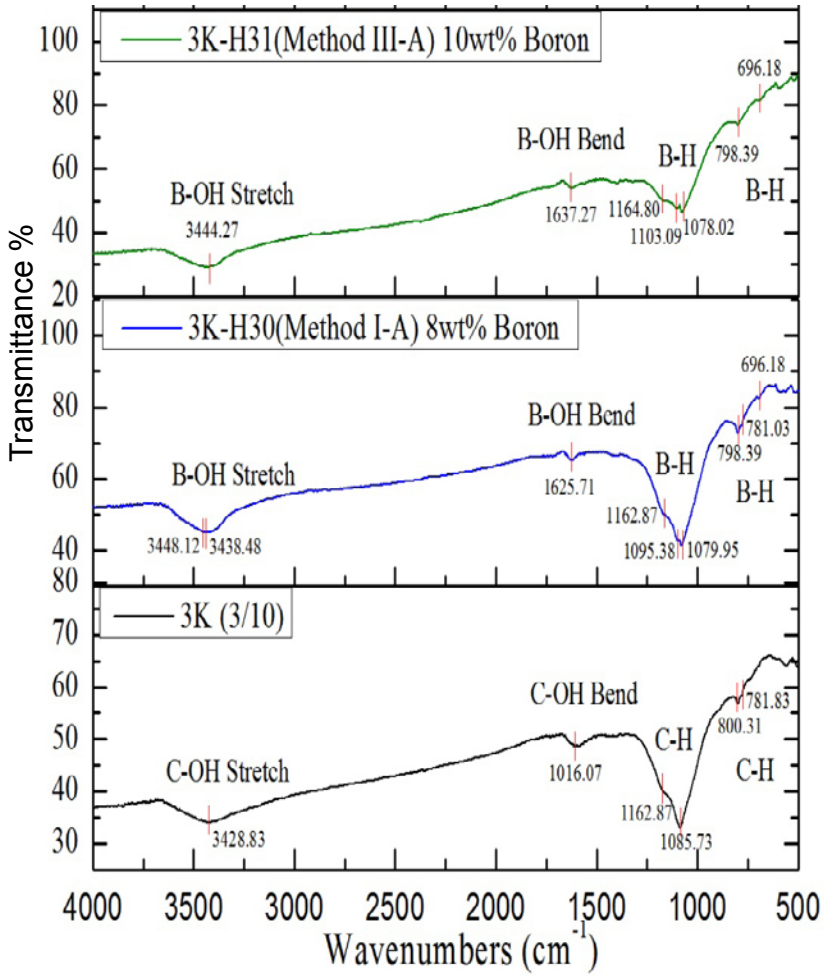


Conclusions:

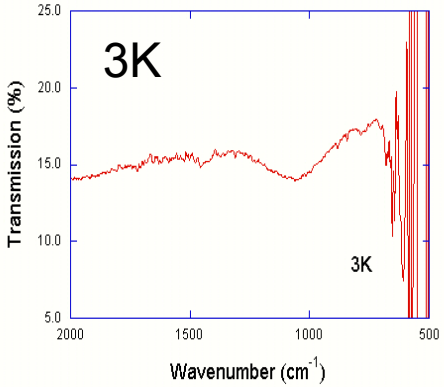
- **Thermodynamic requirement $\partial\Delta h/\partial m_{abs} \leq 0$ gives lower bound for *film thickness l* (exp. film thickness, agrees well with simulations)**
- **Isosteric heats from Clausius-Clapeyron in good agreement with microcalorimetric values**
- **Δh from *absolute adsorption isotherms* works to high *P* (coverage), microcalorimetry only up to 0.5 bar**

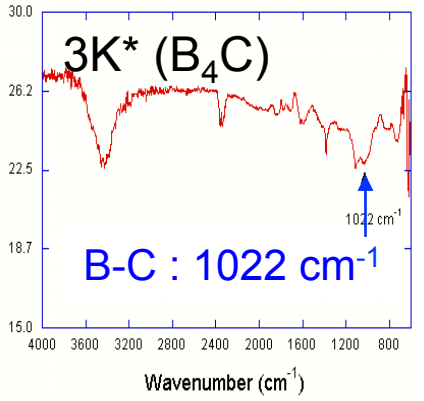
Technical Accomplishments 5 – Observation of B-C bonds by FT-IR

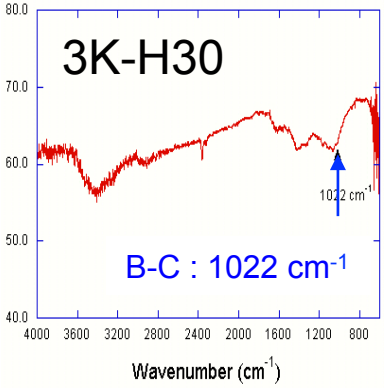
Conventional FTIR method cannot recognize the difference of 3K, 3H30, and 3K-H31 at 1020 cm^{-1} of B-C bond.

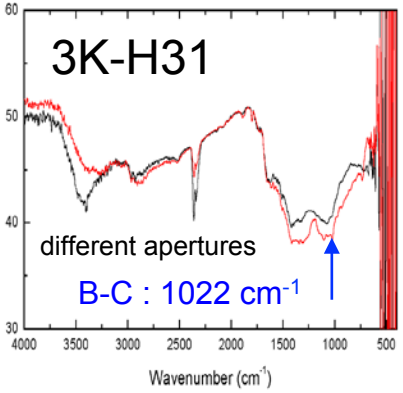


With small apertures, the B-C bond is evident







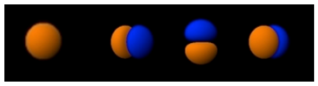


Conclusions:

- **FTIR observation of line at 1022 cm^{-1} characteristic of B-C bonds**
- **First time that the existence of B-C bonds in boron-doped carbons (vapor deposition) has been observed**

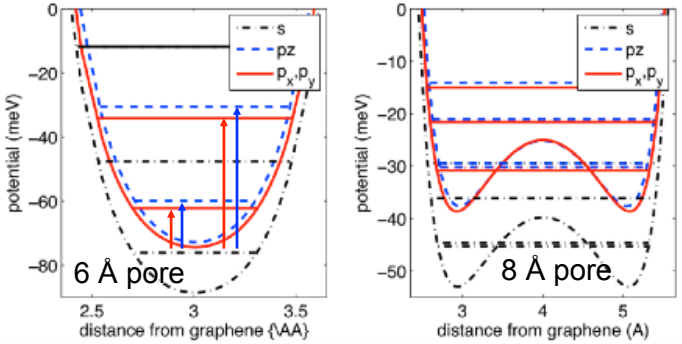
Technical Accomplishments 6 – Incoherent Inelastic Neutron Scattering (IINS)

Theory: sub-nm characterization of pores



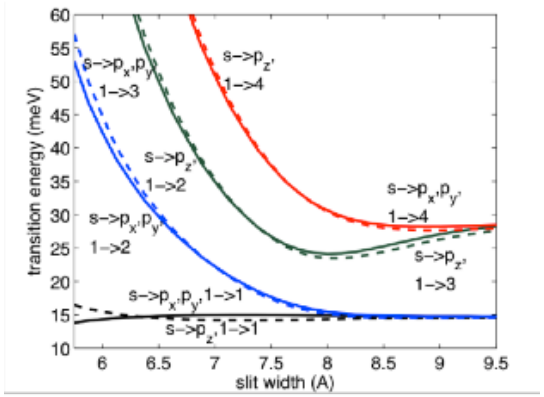
$$E_J = J(J+1)\frac{\hbar^2}{2\mu r^2},$$

$E_1 - E_0$ = 14.7 meV

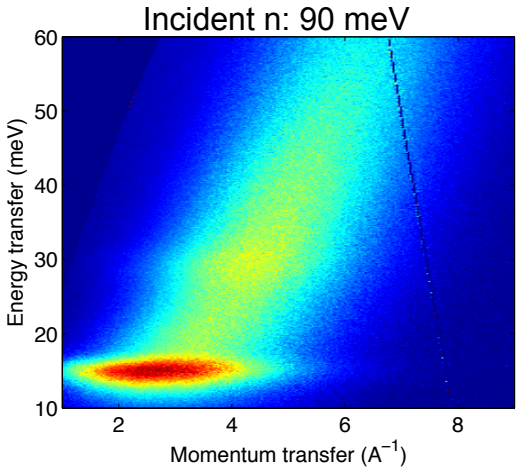


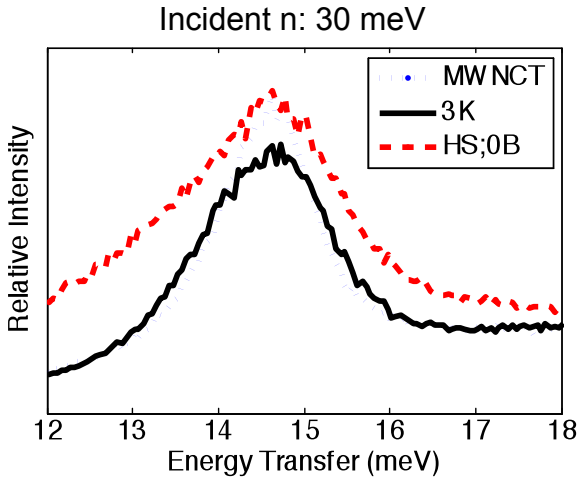
← Quantum levels for adsorbed H_2

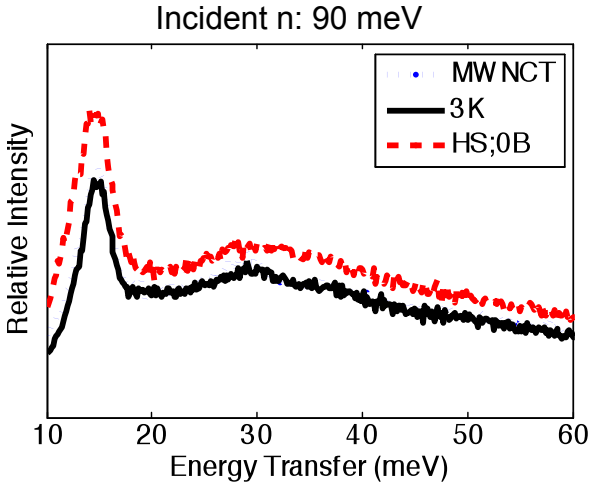
IINS peaks vs. pore width →



Experiment, @ ORNL





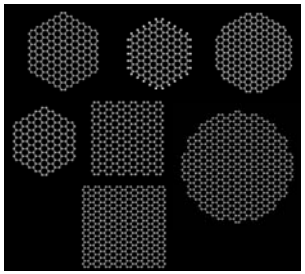


Conclusions:

- **IINS is capable of probing both *energy levels* and *quantum states* of adsorbed H_2 directly.**
- **Experimentally observed 1st rotational transition ($E_1 - E_0$) at 14.7 meV and roto-vibrational peak at 29.5 meV (combination of rotational transition and quantum levels in adsorption potential).**
- **<u>Shows potential for sub-nm pore characterization</u> (alternative to N_2, NMR, …)**
- **Broadening of peaks: in-plane recoil + coupling to phonon modes (still needs analysis)**

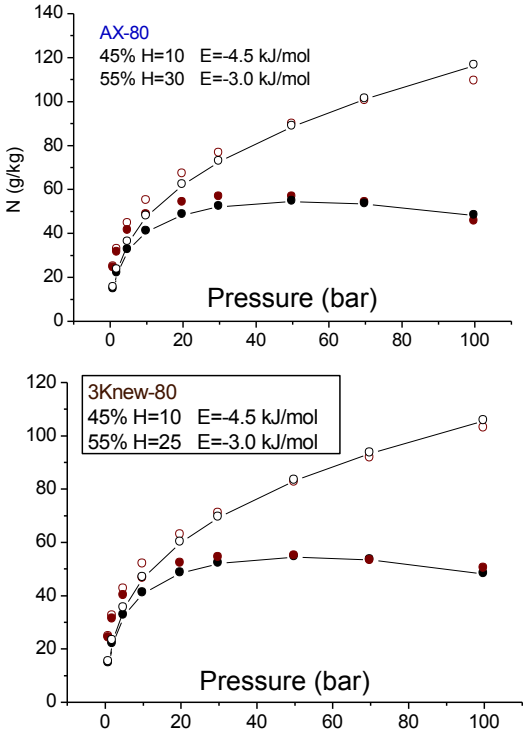
Technical Accomplishments 7 – GCMC Simulations on Non-Traditional Pore Geometries

Search for (a) best representation of experimental isotherms (pore structure & energetics from H_2 ads.); (b) pore structures with max. H_2 storage capacity

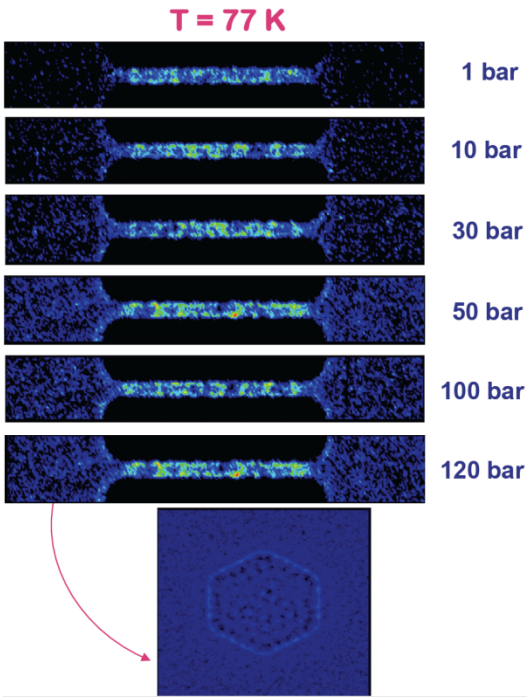


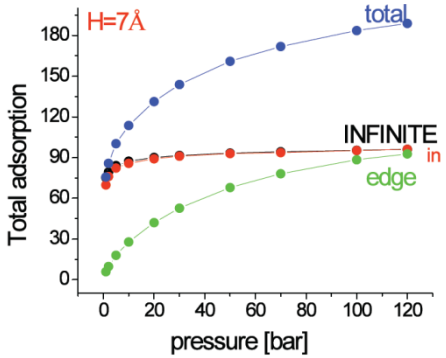
Input:
1. Pore size distribution
2. Pore shape & lateral dimensions
3. Adsorption (binding) energy

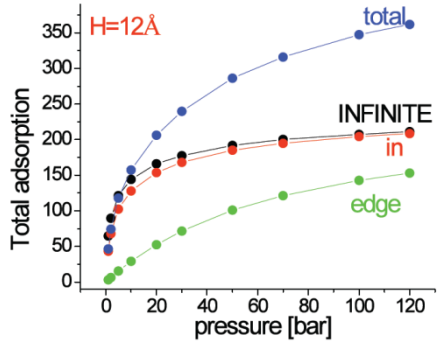
Infinite slit pores, with 2 widths & 2 energies:



Slit pore of width *H* between 2 hexagons of side length 11 Å:







Conclusions:

- **Simultaneous fit of excess ads. & gravim. storage cap. (left panels) constrains pore widths & energies effectively**
- **In finite slit pore, edge ads. ≈ in-plane ads.; doubles gravim. storage cap. relative to infinite pore (right panels)**
  Reason: at edge, there is a large region where ads. Is weaker than in slit, but strong enough to hold H_2 significantly

Collaborations

- **Midwest Research Institute** (Private Sector): Subcontractor for design and construction of instrument for large-scale, automated B-doping (B-doped monoliths)
- **NREL** (Federal): Validation of H_2 uptake data. [L. Simpson, P. Parilla, K. O'Neill]
- **Advanced Photon Source/ANL** (Federal): Collaboration with J. Ilavsky for Ultra-small-angle x-ray scattering studies of samples under General User Program (GUP-10069, GUP-20661).
- **NIST** (Federal): Collaboration with Y. Liu, G. Brown, and J. Burress on small-angle neutron scattering experiments on samples loaded with H_2, including density correlations of nonadsorbed H_2.
- **U. Montpellier II** and **U. Marseille**, France (Academic): Collaboration with L. Firlej and B. Kuchta to perform GCMC simulations.
- **Wroclaw U. Technology**, Poland (Academic): Collaboration with S. Roszak for adsorption potentials for H_2 sorption on B-doped materials from ab initio quantum-chemical computations.
- **ORNL** (Federal): Collaboration with M. Stone, use of beamtime for incoherent inelastic neutron scattering off H_2 adsorbed in nanoporous carbon.
- **U. Provence**, France (Academic): Collaboration with P. Llewellyn for microcalorimetric determination of isosteric heat of adsorption (H_2 adsorbed in nanoporous carbon).
- **U. Missouri** (Academic): Collaboration with P. Yu to perform FTIR experiments on B-doped carbon. Collaboration with H. Taub to analyze IINS experiments.

Future Work: Plans for 2011/12

- Materials development and characterization:
  - Continue production of B-doped samples ($B_{10}H_{14}$) under O_2-free conditions; investigate chemical pathways during pyrolysis of $B_{10}H_{14}$ and annealing (mass spectroscopy of decomposition products) and effects on H_2 storage; optimize pathway of vapor/liquid deposition of $B_{10}H_{14}$ based on phase diagram of $B_{10}H_{14}$; raise surface area of doped samples by removal of B via high-temperature reaction with H_2; optimize annealing
  - Measure FTIR spectra of B-doped samples systematically; find number of B-C bonds per surface area
  - Characterize B-doped materials produced from BCl_3 and compare with B-doping from $B_{10}H_{14}$
  - Determine isosteric heats of B-doped samples at low/high coverage and low/high temperature from corresponding isotherms (Clausius-Clapeyron; Henry's law). Infer distribution of binding energies from analysis (highest/lowest/average binding energy)
  - Determine experimental film thicknesses/densities from Clausius-Clapeyron and compare with values for saturated films, $\rho_{film}(T)$, from high-pressure excess adsorption isotherms (2010 Report), and with values from numerical simulations
- Continue development of IINS, SAXS/USAXS, TEM/SEM methods for characterization of nanopores
- Continue numerical simulations to investigate edge adsorption vs. in-plane adsorption in finite slit pores, and compare results with experimental results on carbons activated at high KOH:C and high *T*. Continue simulations to determine pore structures and energetics from experimental H_2 isotherms
- Complete automated B-doping instrument (MRI); use for vapor deposition of $B_{10}H_{14}$ for B:C = 10 wt%
- Manufacture B-doped monoliths; test in 0.5-liter HTF and 10 liter tank; study flow rate (loading/unloading) and thermal management issues.

Project Summary

- 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 (independent of surface area) at 303 K and 200 bar by 30% relative to undoped material. Indicates increase in *average* binding energy, not solely highest binding energy
- Optimized pore geometry of undoped carbons. Determined that low KOH:C and *T* give large, closely stacked "graphene sheets"; and high KOH:C and *T* give small, loosely stacked "sheets". Optimum geometry: KOH:C = 3.5 and *T* = 800 ^oC; best balance between large fraction of narrow pores and large cumulative pore volume
- Compared monoliths vs. powders (undoped). All briquettes outperform MSC-30 at 300 K in terms of areal excess adsorption (~ average binding energy) and volumetric storage capacity. Best monolith gave 10 g H_2/liter C at 300 K & 100 bar
- Developed method to determine experimental thicknesses of H_2 films from Clausius-Clapeyron analysis of absolute adsorption isotherms. Agree well with simulations. Validated isosteric heats from absolute adsorption isotherms by microcalorimetric measurements.
- Established existence of B-C bonds in B-doped carbons, made from $B_{10}H_{14}$, using FTIR spectroscopy.
- Conducted inelastic neutron scattering experiment to observe rotational-vibrational transition in H_2 adsorbed in sub-nm carbon pores. Proof-of-concept for sub-nm pore characterization.
- In simulations of H_2 adsorption in finite slit pores, found large contributions from edge sites: edge adsorption comparable to in-plane adsorption; doubles gravimetric storage capacity relative to infinite pores