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, 2012
- Percent complete: 30%

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 received in FY09:
  – DOE share: $550K
  – Contractor share: $111K
- Funding for FY 2010
  – DOE share: $550K
  – Contractor share: $227K

Partners

Interactions/collaborations:

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

Objectives & Relevance

Overall

- Fabricate high-surface-area, multiply surface-functionalized nanoporous carbon, from corncob and other precursors, for reversible H_2 storage with superior storage capacity:

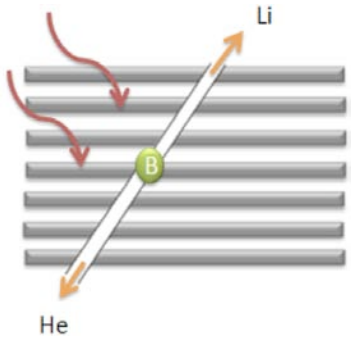
1) Create surface areas ≥ 4500 m^2/g and average binding energy ≥ 12 kJ/mol
2) Functionalize materials with B, Li, …:
   physisorption of H_2 on high-surface-area, high-binding-energy surfaces

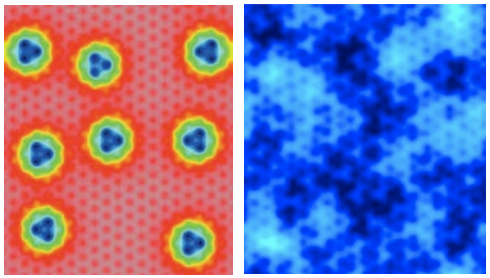
- Characterize materials & demonstrate storage performance

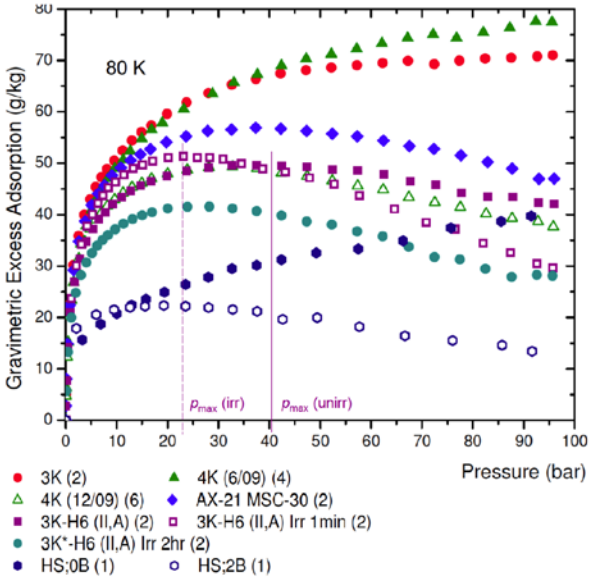
1) Determine pore-space architecture, nature of functionalized sites, H_2 sorption isotherms (1-100 bar), isosteric heats, and kinetics, at 77-300 K
2) Develop theoretical predictions of binding energies and H_2 sorption isotherms in B-substituted materials and engineered nanospaces (structure-function relations)
3) Use structure-function relations to understand storage performance of materials in terms of distributions of binding energies and pore widths

- Optimize pore architecture and composition

1) Use structure-function relations to optimize gravimetric and volumetric storage capacities
2) Compare B-functionalized materials produced by different synthetic methods
3) Fabricate monoliths of optimized materials; determine storage capacities and charge/discharge kinetics under conditions comparable to an on-board H_2 tank
4) Reach target of 60 g H_2/kg carbon and 45 g H_2/liter carbon (~2015 DOE target) at 50 bar and 300 K, on monoliths





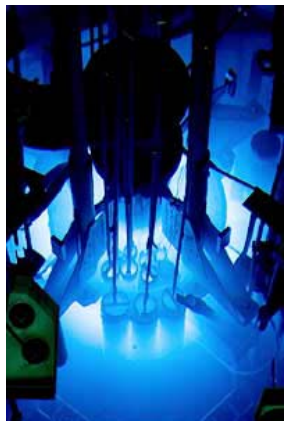


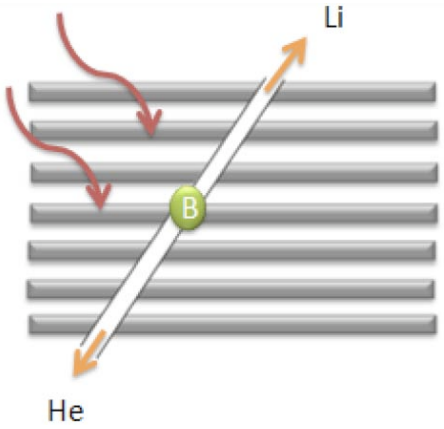
Approach—I

- Maximize surface area
  ('Engineered Nanospaces I')
  - High-surface area carbon from corncob: S_i ~ 3000 m^2/g
  - Substitute with B and create additional surface area by boron neutron capture, fission into Li and alpha particle,

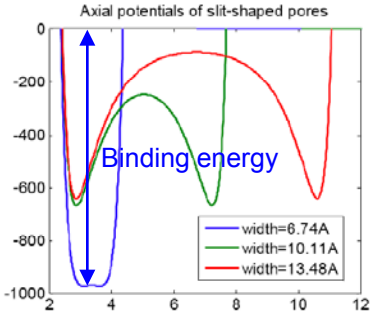
    $^{10}B + {}^{1}n \rightarrow [^{11}B] \rightarrow {}^{7}Li + {}^{4}He + \gamma + 2.4$ MeV

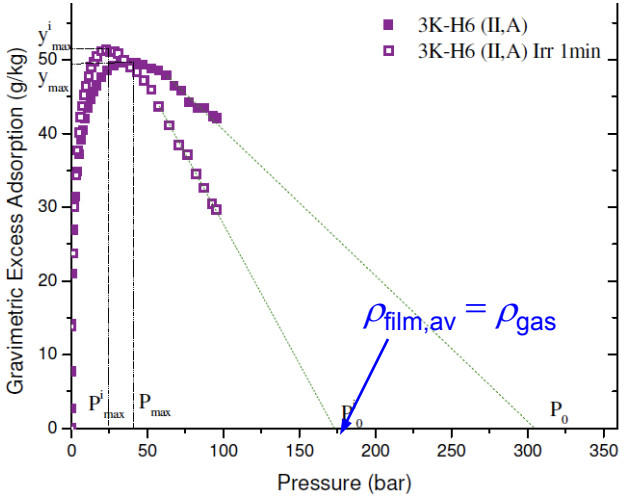
    (U. Missouri Research Reactor), and etching of fission tracks
  - Theor. optimum track width: w ~ 1 nm
    Theor. max. surf. area: $S_f = 2S_i$ ~ 6000 m^2/g



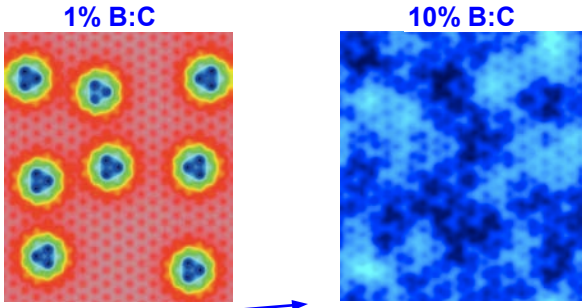


- Create nanopores
  Raises H_2 binding energy
  ('Engineered Nanospaces II')
  In narrow pores, adsorption potentials overlap and create deep energy wells:
  Binding energy in wide pore: 5 kJ/mol
  Binding energy in narrow pore: ~9 kJ/moll
  Expect: $\rho_{film,\ narrow\ pore} >> \rho_{film,\ wide\ pore} >> \rho_{gas}$

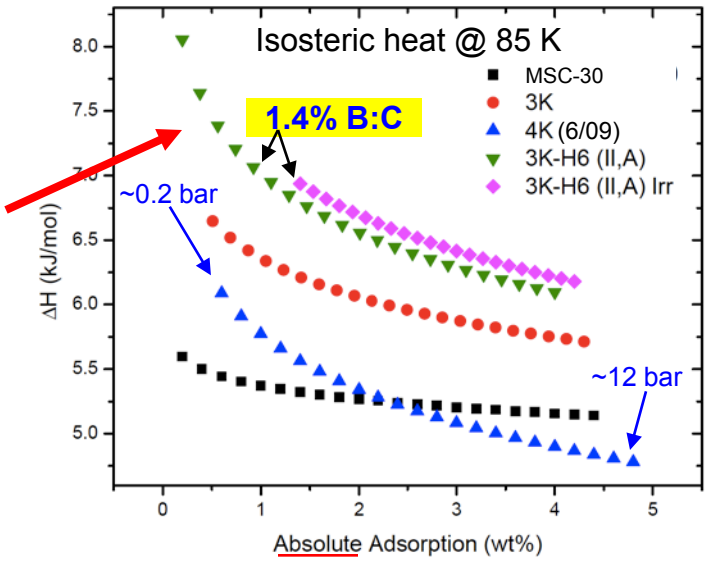




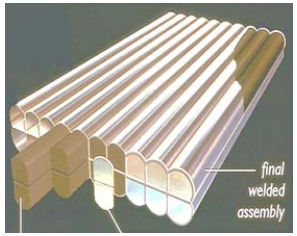
Approach—II



- Surface functionalization with B/Li/… ('Substituted Materials')
  Raises H_2 binding energy further
  - Substitute 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)
    Twofold use of B: (a) boron neutron capture;
    (b) remaining B increases binding energy
  - Compute adsorption potentials (QC) and simulate H_2 adsorption (GCMC, MD) to analyze exp. isotherms in terms of distributions of binding energies and pore widths
  - Isosteric heats confirm that B-doping raises binding energy (preliminary results)



- Manufacture monoliths for conformable, lightweight tank
  - Minimizes wide pores; minimizes tank volume
  - Low pressure, 50 bar: enables conformable tank design
  - High binding energy, 15 kJ/mol: enables storage at 300 K



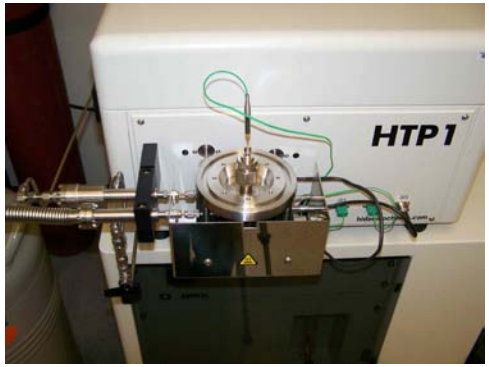
Approach—III: Tasks

Task	Progress Notes	% Comp
1. Fabricate functionalized carbons		
– Fabricate B-doped materials by vapor deposition & thermolysis of decaborane	Achieved. Samples characterized. Optimization of materials pending	80%
– Create fission tracks by boron neutron capture (BNC)	On track. Pending: variety of samples	80%
– Create new surface area by etching of fission tracks	N_2 and SAXS find no significant difference (surf. area, pore structure) between irradiated and unirrad. material. But irradiated samples show very different H_2 isotherms, considerably higher binding energy. Pending: etching	50%
– Pressing of carbon into monoliths	Not started	0%
– Pore drilling	Achieved with BNC; also by expulsion of HCl during pyrolysis of PVDC	20%
2. Fabricate hybrid materials	Not started	0%
3. Characterize and optimize materials/H_2 storage performance		
– Map pores space by SAXS, N_2 adsorption, H_2 adsorption, SEM/TEM	SAXS methodology for nanopore analysis complete (shape, width, length, wall thickness, porosity) and applied to numerous samples; N_2 BET routinely performed; H_2 newly developed; SEM/TEM performed on select systems	60%
– Predict H_2 isotherms in pure-C and B-substituted materials and compare with exp. isotherms	GCMC and MD simulations of H_2 isotherms complete for simple geometries and applied to select experimental systems; QC computations of adsorption potential for select B configurations complete	60%
– Measure H_2 binding energies from adsorption isotherms	Developed method, based on absolute adsorption, to determine isosteric heats at high coverage. Applied to pure-C and B-substituted materials. Best result: $E_{B,av}$ = 9-11 kJ/mol on B:C =1.4 wt%	50%
– Compare different methods of B functionalization	Compared structure and H_2 sorption of B-doping by decaborane vs. copolymerization	30%
– Optimize gravimetric & volumetric storage capacities	Developed quantitative relation between gravim. and volum. capacity at constant gravim. excess ads. (variable porosity, B:C content, …)	70%
– Design test vessel for monoliths	Not started	0%
4. Characterize and optimize monoliths		
– Construct test vessel for monoliths	Not started	0%
– Validate and optimize monoliths	Not started	0%

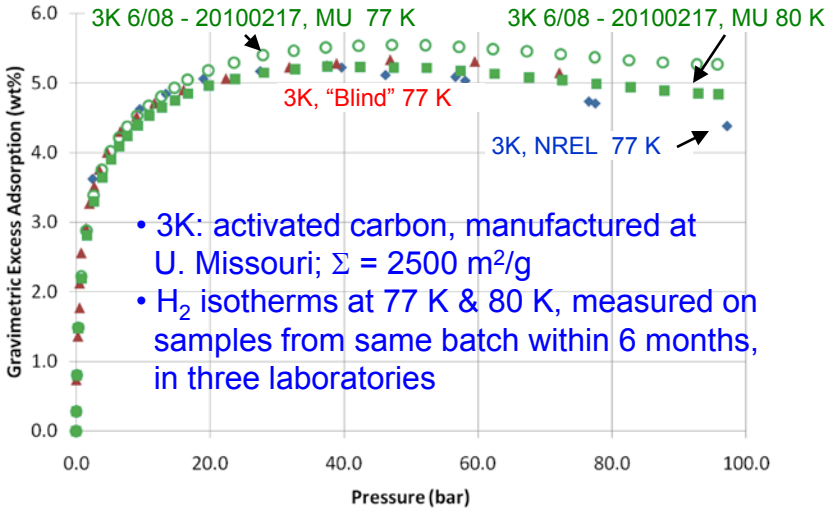
Materials synthesis/performance I

Validation of H_2 isotherms in independent laboratories

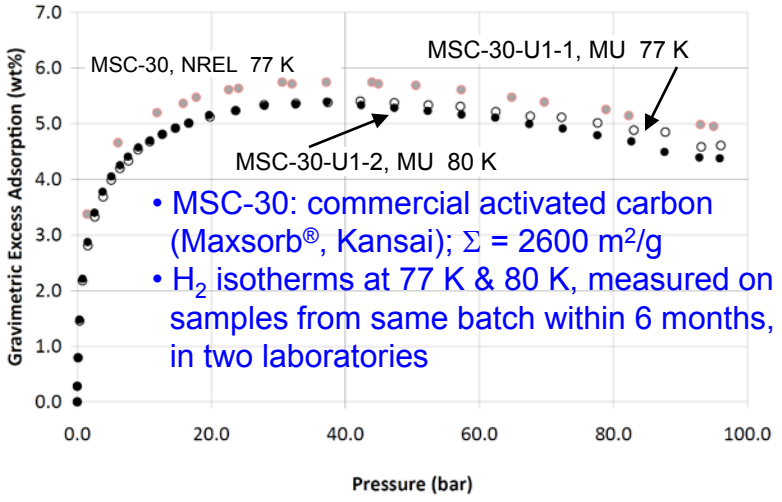
- U. Missouri: Hiden HTP1 volumetric analyzer (p = 1-100 bar, T = 77-775 K)
- NREL: Hy-Energy PCTPro-2000 volumetric analyzer
- "Blind": Independent analysis in another laboratory



Gibbs excess adsorption:
$m_{H2}/(m_{H2} + m_{carbon})$



- 3K: activated carbon, manufactured at U. Missouri; Σ = 2500 m^2/g
- H_2 isotherms at 77 K & 80 K, measured on samples from same batch within 6 months, in three laboratories



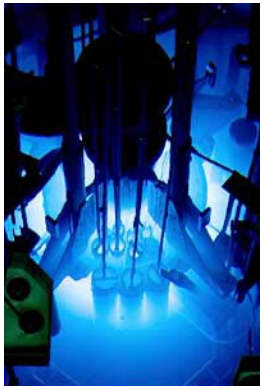
- MSC-30: commercial activated carbon (Maxsorb®, Kansai); Σ = 2600 m^2/g
- H_2 isotherms at 77 K & 80 K, measured on samples from same batch within 6 months, in two laboratories

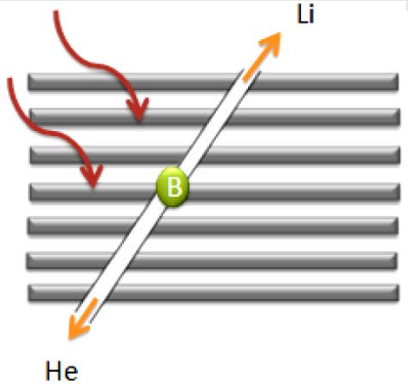
Conclusions:

- **Validation of HTP1 calibration and operation:**
  - **MU sample 3K measured in 3 independent labs: agreement within ~ 5%**
  - **"Reference sample" MSC-30 measured in 2 labs: agreement within ~ 5%**
- **Uniform materials & repeatable production within ~5%**
- **H_2 uptake at 77 & 80 K differs by as much as 10%. (Equilibration is faster at 80K on HTP1.)**

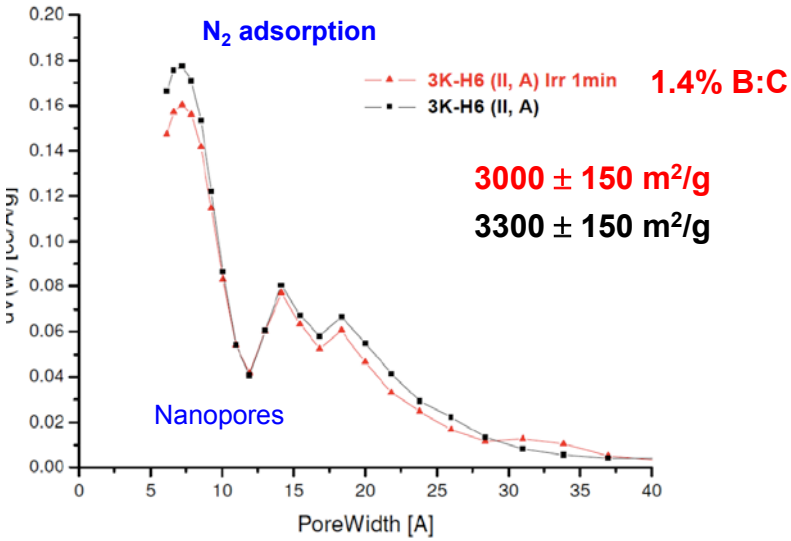
Materials synthesis/performance II: B-doping & neutron irradiation (Part 1)

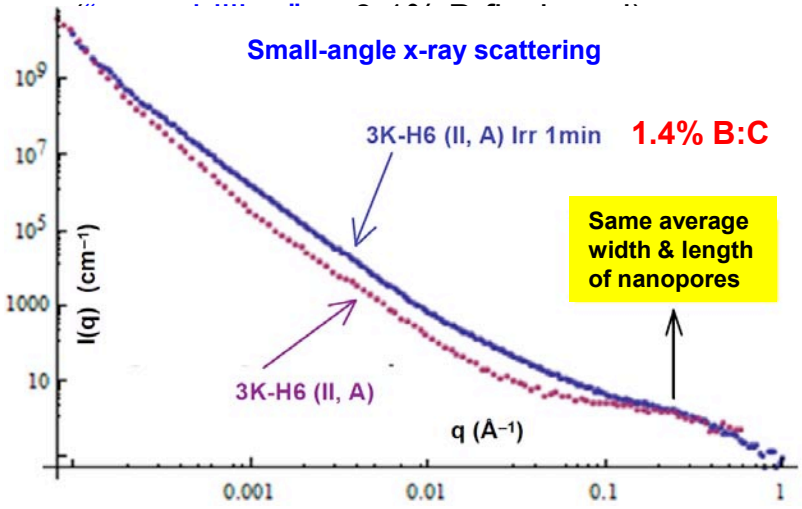
+ B





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





Conclusions:

- No significant difference between irrad./unirrad. material according to N_2 & SAXS
- But significant difference in hydrogen adsorption (next slide)

Materials synthesis/performance II: B-doping & neutron irradiation (Part 2)

But H_2 adsorption is significantly different on irradiated material

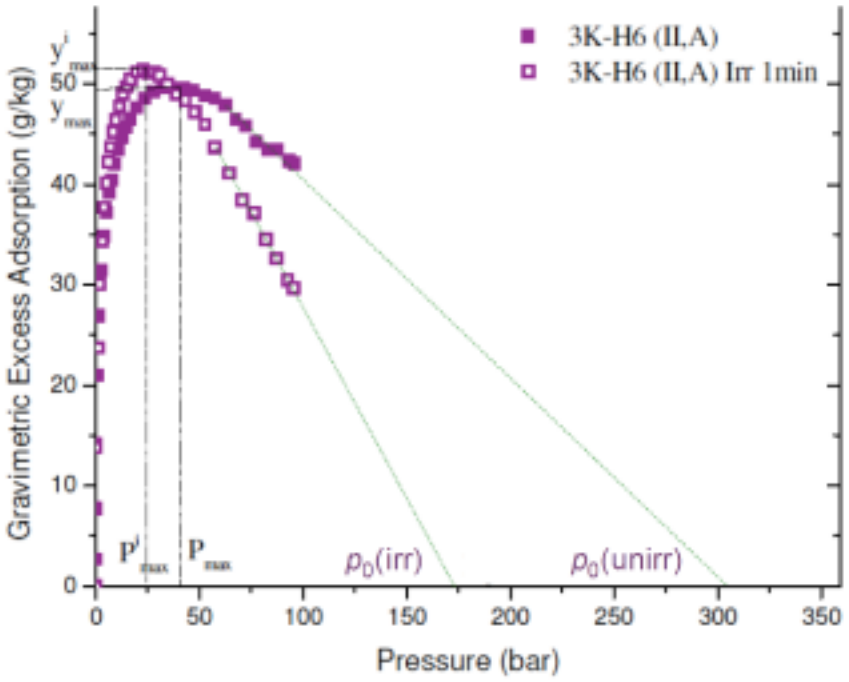
- Energetic and geom. structure from excess adsorption @ 80 K
- Local max. of G_{ex}: on high-pressure side, density of gas grows faster than density of adsorbed film; ads. film ~ incompressible
- Local max. at low pressure: high average binding energy, $E_{B,av}$ Pressure at local max., $p_{max}(T)$, gives $E_{B,av}$
- Pressure at which $G_{ex}= 0$, $p_0(T)$, gives density of saturated film, $\rho_{film}(T)$
- Slope $\partial G_{ex}/\partial p$ at $p >> p_{max}$ gives specif. surf. area as seen by H_2 @ 80 K, Σ_{H2} (Aranovich & Donohue, 1997)
- Quantitatively:

$\rho_{film}(T) = m_{H2}\, p_0(T)/(kT)$ Mass density of sat. film

$[n_{film}(T)]^{-1/3} = [p_0(T)/(kT)]^{-1/3}$ Diameter of H_2 in sat. film

$\Sigma_{H2} = (-\partial G_{ex}/\partial p)[(kT)^2\, p_0(T)]^{1/3}/m_{H2}$

$\exp(E_{B,av}/(N_A kT)) = [(p_0(T) - 2p_{max}(T))/p_{max}(T)^2]$
$\cdot[\sinh(h\nu/(2kT)]^3 \cdot[(8\pi m_{H2})^3 (kT)^5/h^6]^{1/2}$



Conclusions:

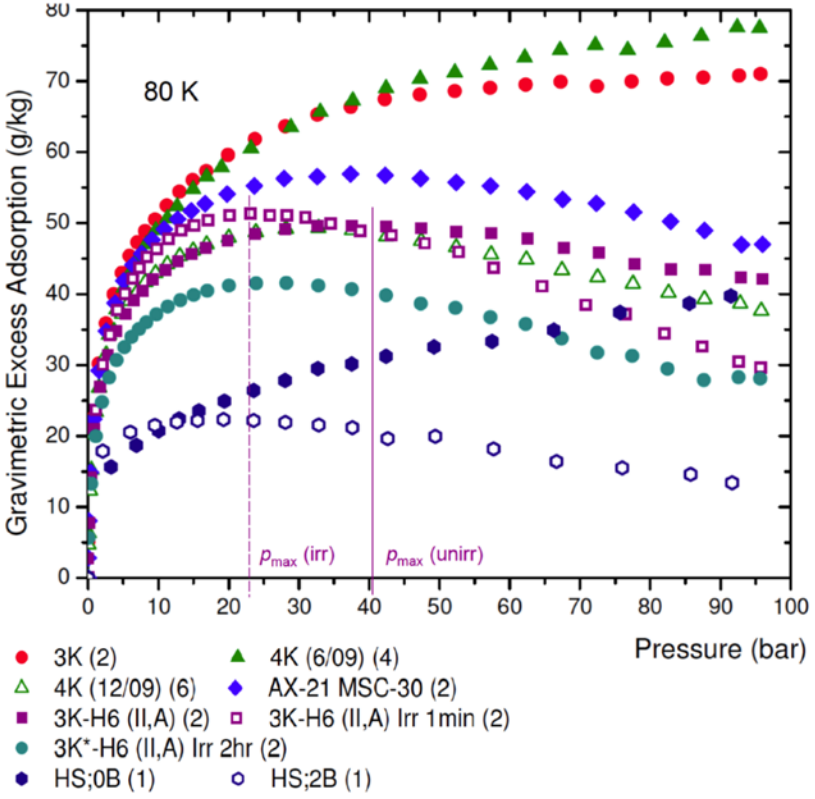
- **Irradiated material hosts lower ρ_{film} and higher $E_{B,av}$ than unirradiated parent material**
- **Hypothesis: – High $E_{B,av}$ due to surface defects created by fission products**
  – Low ρ_{film} due to film discontinuities at edges of newly created pores (fission tracks)
- **FY 2010/11: – Does H_2 see same surface area as N_2 and x-rays (next slide)?**
  – Etching of fission tracks; parametric studies of dependence on B conc. and parent material

Materials synthesis/performance II: B-doping & neutron irradiation (Aux)

Reaction	Product	B:C	Notes
Char + KOH [ratio 1:3, 800 °C]	3K	0.0 wt%	Reactor: stainless steel Product: ~1% Fe, Cr
Char + KOH [ratio 1:3, 800 °C]	3K*	0.0 wt%	Reactor: alumina Product: ~1% Al
"3K" + $B_{10}H_{14}$	3K-H6 (II,A)	1.4 wt%	B-H decomp., 600 °C
"3K*" + $B_{10}H_{14}$	3K*-H6 (II,A)	1.9 wt%	B-H decomp., 600 °C
1 min irradiation	3K-H6 (II,A) Irr 1min	1.4 wt%	$^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He$, + long-lived ^{51}Cr
2 hr irradiation	3K*-H6 (II,A) Irr 2hr	1.9 wt%	$^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He$, < 1 μCi radioactivity

Sample	p_0 (bar)	p_{max} (bar)	$(n_{film})^{-1/3}$ (Å)	ρ_{film} (g/cm^3)	Σ_{H2} (m^2/g), Σ_{N2} (m^2/g)	$E_{B,av}$ (kJ/mol) [a]
MSC-30	360	~40	3.1	0.11	2300, 2600	6.4
4K (12/09)	270	33	3.4	0.08	2100, 2700	6.4
3K-H6 (II,A)	300	~40	3.3	0.09	2200,[b] 3300	6.2 [10.9]
3K-H6 (II,A) Irr 1min	160	23	4.1	0.05	3100, 3000	6.5 [11.2]
3K*-H6 (II,A) Irr 2hr	190	24	3.9	0.06	2300, 2900	6.6 [11.3]
HS:2B	190	21	3.9	0.06	1200, 600	6.9 [11.5]
H_2 gas, 80 K & 50 bar	–	–	–	0.016	–	–

[a]) With v for H_2-graphite potential [with v estimated for H_2-B/C potential]
[b]) Uncertain due to uncertainty in extrapolation to high pressure

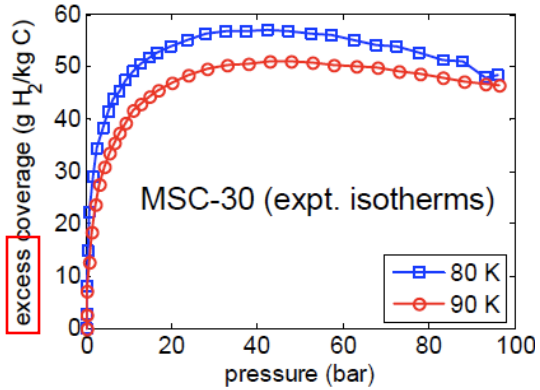


Conclusions:

- **H_2 appears to see same surface area as N_2 in general, but area depends on 'footprint' of H_2 molecule**
- **FY 2010/11: Investigate pressure/temperature/sample dependence of footprint**
- **Density of adsorbed H_2 at 80 K & 50 bar is 3-8 times the density of H_2 gas**

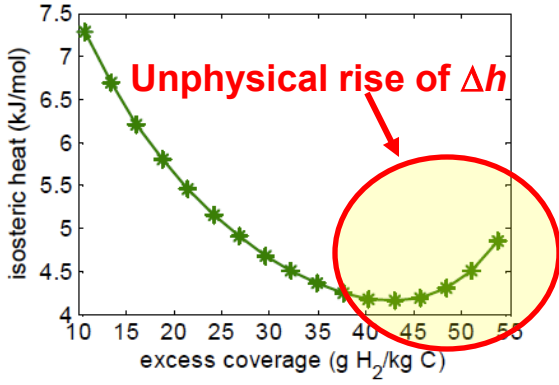
Materials synthesis/performance II: B-doping & neutron irradiation (Part 3)

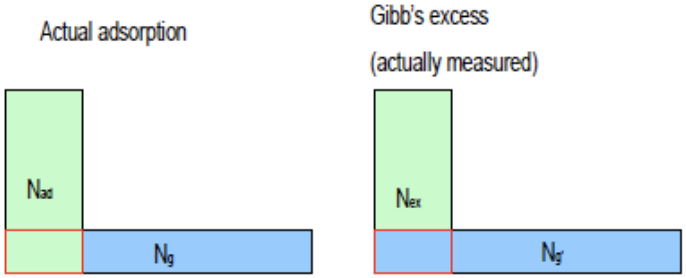
Experimental determination of isosteric heats at medium-to-high coverage/pressure



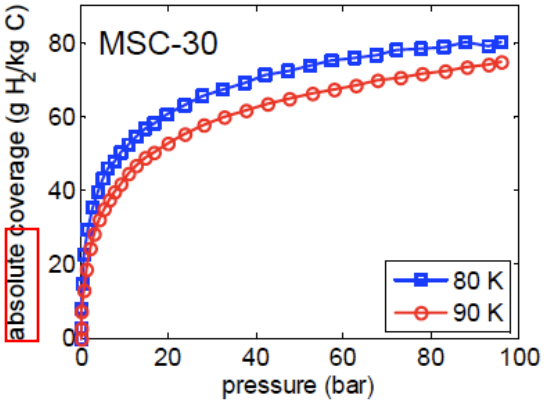
Clausius-Clapeyron Eq.:

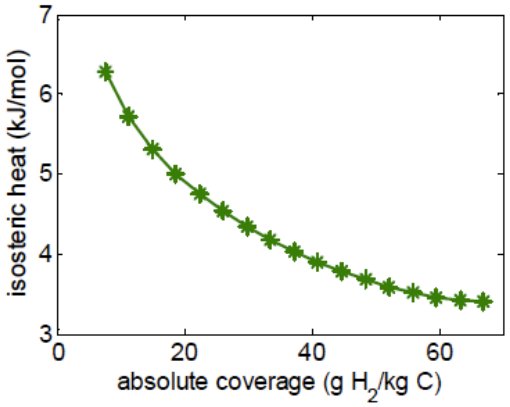
$$\Delta h = \frac{RT_1T_2}{T_2 - T_1}\ln\left(\frac{P_2}{P_1}\right)$$





$$N_{ad} - N_{ex} = V_{film}\rho_{gas}(P,T) = At\frac{P}{kT}$$





Conclusions:

- **Except for very low coverages, compute isosteric heat from *absolute adsorption* instead of *excess*.**
- **Computer simulations provide required microscopic information on film volume and/or thickness.**
- **Product: isosteric heats valid at *all* pressures and coverages.**

Materials synthesis/performance II: B-doping & neutron irradiation (Part 4)

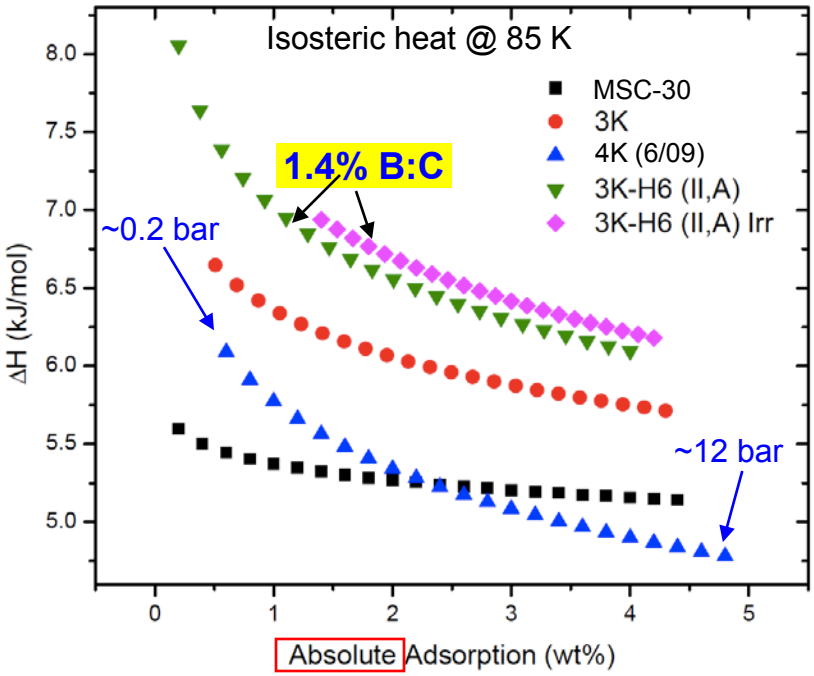
Isosteric heat and binding energies

Comparison of $E_{B,av}$ energy from local max. of excess ads. with estimate of binding energy from isosteric heat

- E_B = ΔH + zero-point/thermal energies = ΔH + (3-5 kJ/mol)
  For 3K-H6 (II,A), B:C = 1.4 wt%: E_B = 10-12 kJ/mol, @ H_2:C = 1 wt%
  For MSC-30, B:C = 0.0 wt%: E_B = 8.5-10.5 kJ/mol, @ H_2:C = 5 wt%
  For 4K (6/09), B:C = 0.0 wt%: E_B = 7.5-9.5 kJ/mol, @ H_2:C = 5 wt%

Sample	B:C (wt%)	$\Sigma_{N2,77K}$ (m^2/g)	$\Sigma_{H2,80K}$ (m^2/g)	Dominant pore size (nm)	G_{ex} (kg/kg, 80 K, 50 bar)	$G_{ex}/\Sigma_{N2,77K}$ ($\mu g/m^2$, 80 K, 50 bar)[a]	Dominant E_B (kJ/mol)
MSC-30	0.0	2600	2300	0.7, 2.0[b]	0.056	21	8-10[d]
4K (6/09)	0.0	2600	N/A	0.7-2.0[b]	0.071	27	7-9[d]
3K-H6 (II,A)	1.4	3300	2200	0.7, 1.5[b]	0.049	15	9-11[d]
3K-H6 (II,A) Irr 1min	1.4	3000	3100	0.7, 1.5[b]	0.047	16	9-11[d,f]
HS;0B	0.0	700	N/A	0.8[c]	0.033	47	~9[e]
HS;2B	1.7	600	1200	0.7[c]	0.020	33	>9[f]

[a] Chahine rule: 20 $\mu g/m^2$ [b] Bimodal [c] Unimodal [d] From ΔH [e] From G_{ex}/Σ [f] From p_{max}

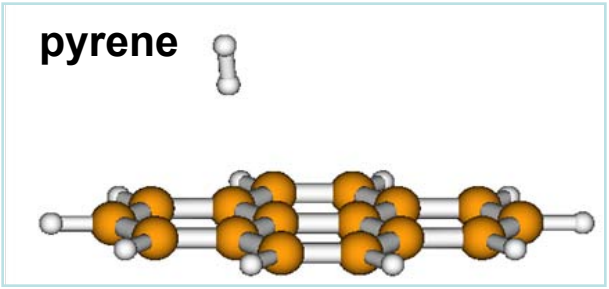


Conclusions:

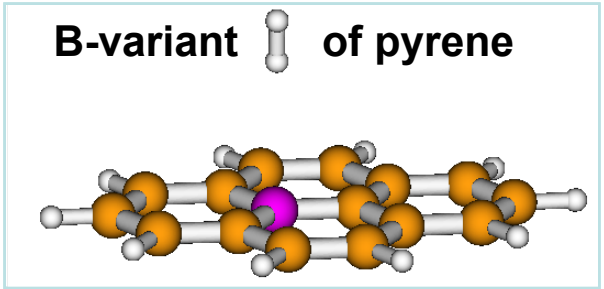
- **B-doping raises binding energy to ~9-11 kJ/mol (conclusion supports theoretical results, see next slide)**
- **Binding energies from local max. of excess ads. agree, within exp. uncertainty, with those from isosteric heat**
- **Isosteric heat of irrad. material is incrementally higher than parent material**

Ab initio + GCMC results for B-substituted carbon (Part 1)

Minimal energies from *ab initio* calculations



Graphene → E_a= 5.16 kJ/mol



Graphene - B → E_a= 7.8 kJ/mol ("over B")

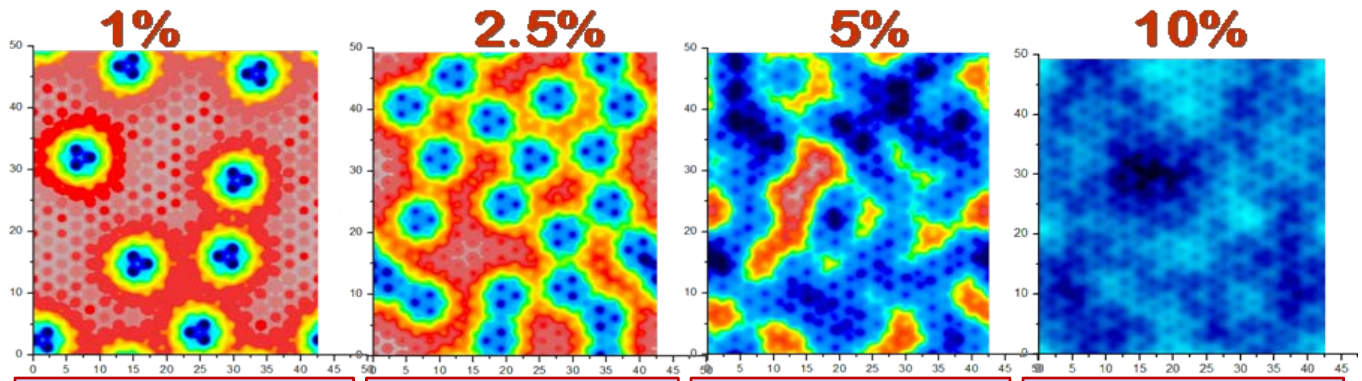
R_{H2-B} = 3.12 Å

E_a= 5.56 kJ/mol ("over nn C")

R_{H2-C} = 3.24 Å

- external frame frozen
- 2nd order Møller-Plesset (MP2) perturbation theory
- restricted open Hartree-Fock wavefunctions
- effective core potential SBKJC VDZ basis set + polarization functions (B,C: *d*; H: *p*)
- All the calculations were carried out using the GAUSSIAN 03 suite of codes.
- MP2 treatment more reliable than DFT (MP2 accurate within ~5%)

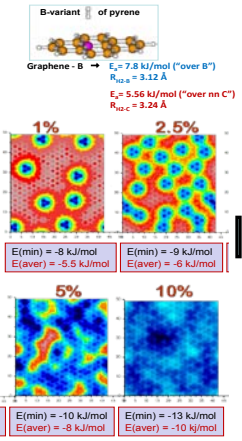
"Additive" approximation: results for B-doped graphene (for B:C > 10%, need aromatic molecule larger than pyrene)



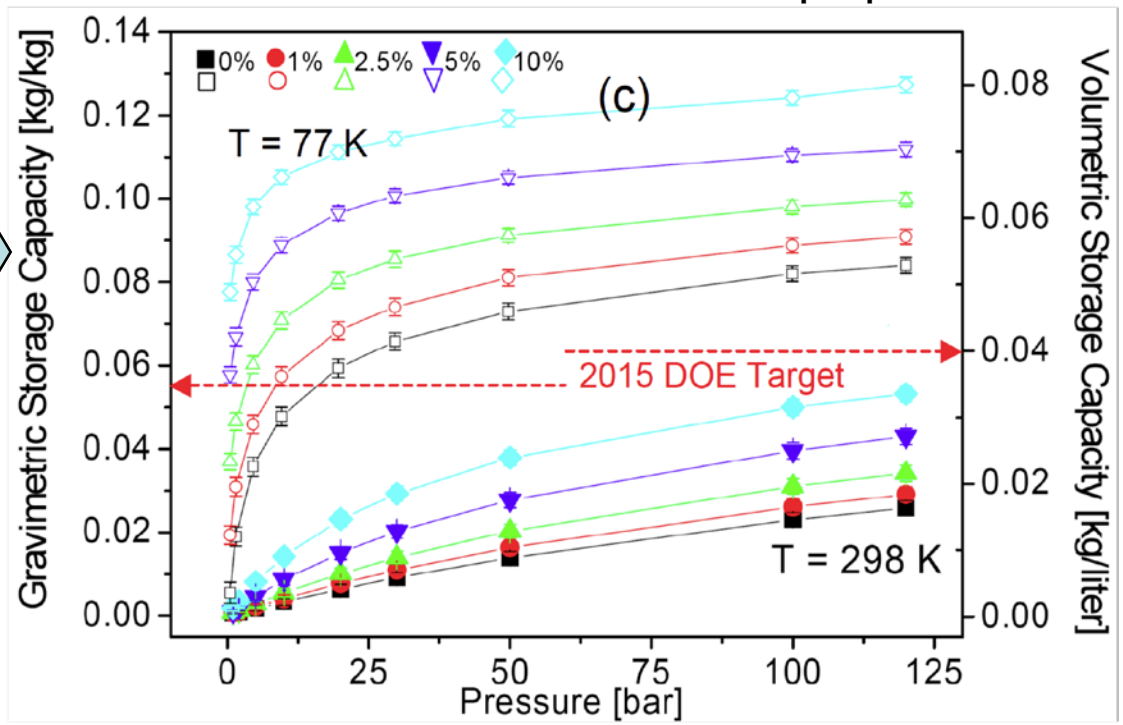
1%	2.5%	5%	10%
E(min) = -8 kJ/mol E(aver) = -5.5 kJ/mol	E(min) = -9 kJ/mol E(aver) = -6 kJ/mol	E(min) = -10 kJ/mol E(aver) = -8 kJ/mol	E(min) = -13 kJ/mol E(aver) = -10 kj/mol

Ab initio + GCMC results for B-substituted carbon (Part 2)

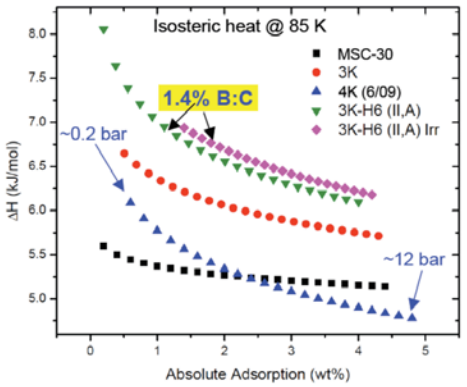
Grand Canonical Monte Carlo Simulations ➔ adsorption isotherms



1.2 nm slit-shaped pore



Experiment:



Conclusions:

- *Ab initio* calculations of H_2 on boron-substituted carbon predict high binding energy. At 10% B, binding energy is raised from ~5 to **~10 kJ/mol** (13.5 kJ/mol at small coverage, decreasing to 6 kJ/mol at high coverage). Is supported by experiments.
- Reversible (***delivery* ~ 97%**) storage of H_2: **~5 wt.%**, **~35 g/l**, close to DOE 2015 targets (5.5 wt.%, 40 g/l) at room temperature and moderate pressures (100 bar), excluding support equipment.

Materials synthesis/performance III: excess adsorption and storage capacities at 80 & 300 K

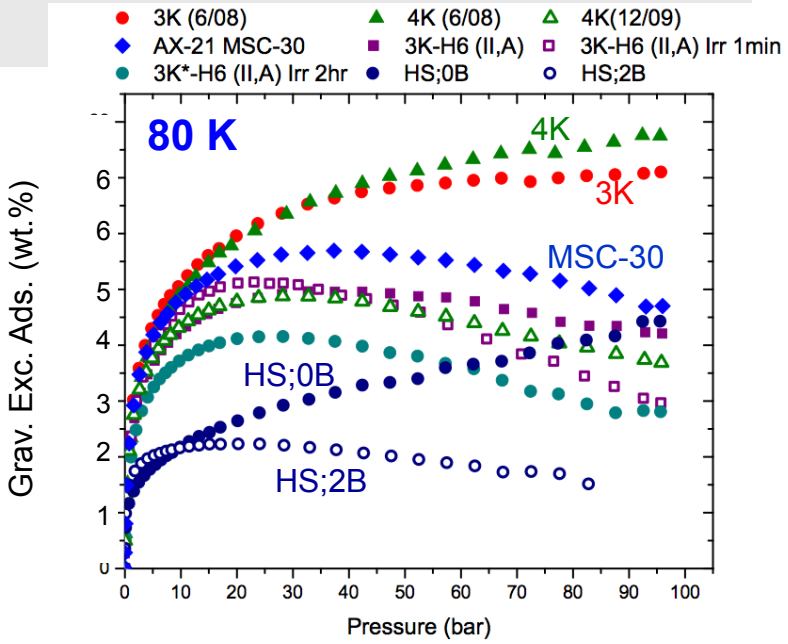
Best performing material at 80 K:

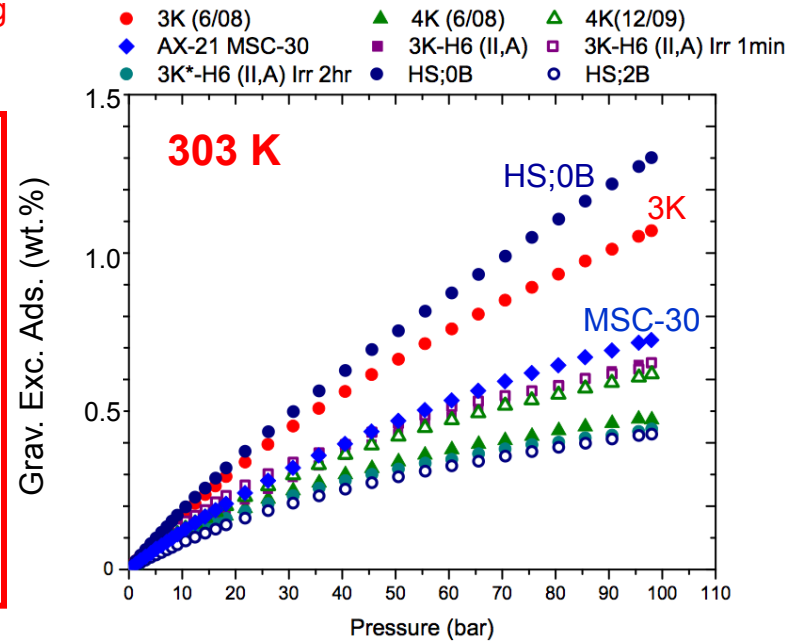
- Excess adsorption (wt.%):
  - 4K & 3K (B:C = 0).
  - Reason: large surf. area, multilayer adsorption
- Areal excess adsorption (g/m^2):
  - HS;0B (B:C = 0), at high P
  - HS;2B (B:C = 1.7 wt%), at low P
  - Both ~ twice "Chahine value"
  - (HS;0B & HS;2B from another project)

Best performing material at 303 K:

HS;0B (B:C = 0), even though it has small Σ ~ 700 m^2/g

3K close second, but with high Σ ~ 2500 m^2/g





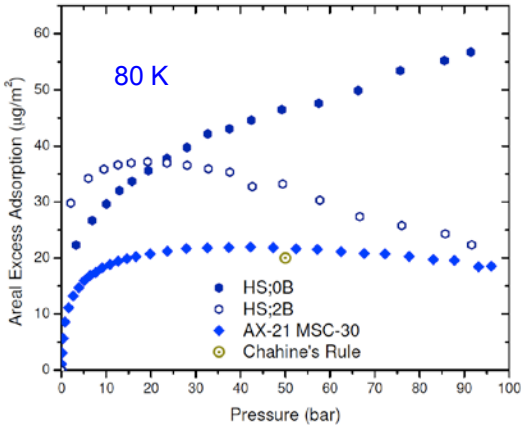
Conclusions:

- **Exceptional performance of HS;0B and HS;2B**
  Record excess ads. of HS;0B at room temperature
- **Can this be increased by further activation/pore-drilling?**
- **Hypothesis (80 K):**
  - **HS;0B: Very high ρ_{film} in smooth, <0.7 nm pores; low $E_{B,av}$ (shifts p_{max} to high pressures)**
  - **HS;2B: High ρ_{film} in smooth, <0.7 nm pores; high $E_{B,av}$ (shifts p_{max} to low pressures)**
- **B-doping raises $E_{B,av}$**

Materials synthesis/performance III: excess adsorption and storage capacities at 80 & 300 K (Aux)

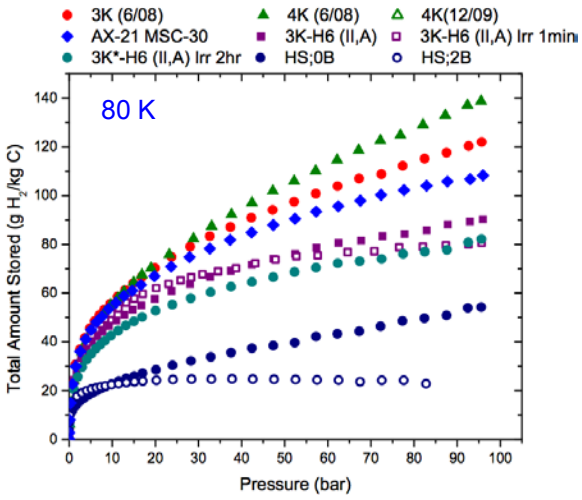
Best performing material at 80 K:

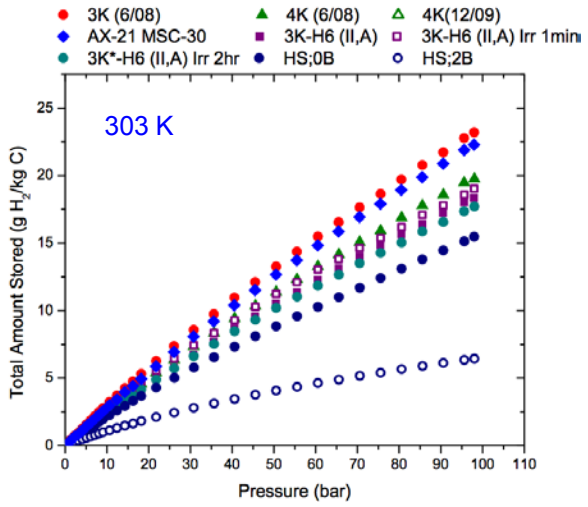
- In terms of gravim. storage cap.: 4K (B:C = 0). Reason: large surf. area, multilayer adsorption
- In terms of areal excess adsorption: HS;2B (B:C = 1.7 wt%) & HS;0B (B:C = 0) Both ~ twice "Chahine value"



Best performing material at 303 K:

- In terms of gravim. storage cap.: 3K (B:C = 0); H_2:C = 2.3 wt% at 100 bar
- In terms of areal excess adsorption: HS;0B (B:C = 0) ~ 4 times value of 3K





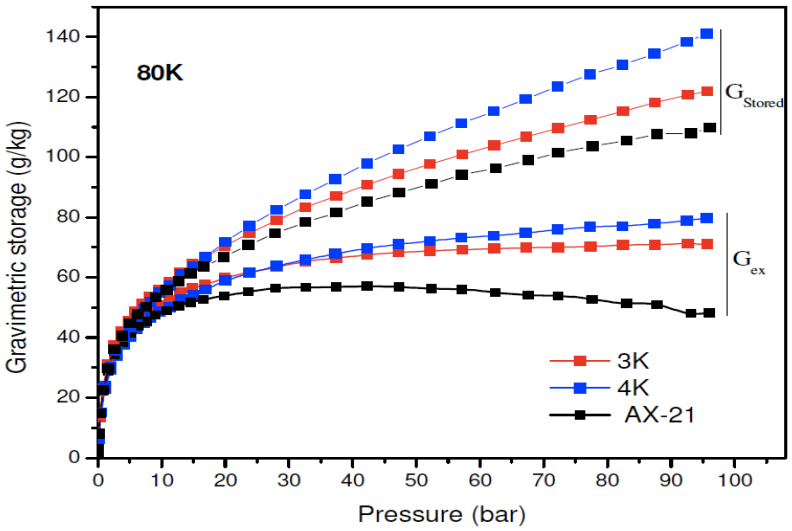
Storage capacities calculated with intragranular porosity of material

Sample	B:C (wt%)	$\Sigma_{N2,\ 77\ K}$ (m^2/g)	$\Sigma_{H2,\ 80\ K}$ (m^2/g)	Dominant pore size (nm)	G_{ex} (kg/kg, 80 K, 50 bar)	$G_{ex}/\Sigma_{N2,\ 77\ K}$ ($\mu g/m^2$, 80 K, 50 bar)[a]	Dominant E_B (kJ/mol)
MSC-30	0.0	2600	2300	0.7, 2.0[b]	0.056	21	8-10[d]
4K (6/09)	0.0	2600	N/A	0.7-2.0[b]	0.071	27	7-9[d]
3K-H6 (II,A)	1.4	3300	2200	0.7, 1.5[b]	0.049	15	9-11[d]
3K-H6 (II,A) Irr 1min	1.4	3000	3100	0.7, 1.5[b]	0.047	16	9-11[d,f]
HS;0B	0.0	700	N/A	0.8[c]	0.033	47	~9[e]
HS;2B	1.7	600	1200	0.7[c]	0.020	33	>9[f]

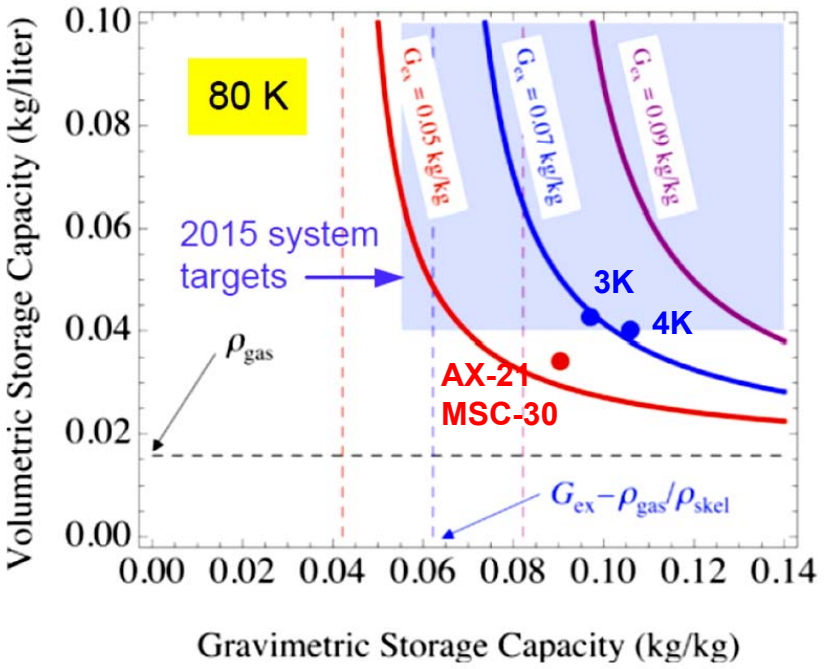
[a] Chahine rule: 20 $\mu g/m^2$ [b] Bimodal [c] Unimodal [d] From ΔH [e] From G_{ex}/Σ [f] From p_{max}

This slide serves as supporting data for previous slide

Materials synthesis/performance IV: gravimetric vs. volumetric storage capacity



	AX-21 MSC-30	3K	4K
Ratio KOH:C for chemical activation	N/A	3:1	4:1
Specific surface area (Σ)	2,600 m^2/g	2,500 m^2/g	2,600 m^2/g
Porosity (ϕ)	0.81	0.78	0.81
Gravim. H_2 excess (G_{ex}; 80 K, 50 bar)	0.057 kg/kg	0.069 kg/kg	0.073 kg/kg
Gravim. H_2 stored (G_{st}; 80 K, 50 bar)	0.090 kg/kg	0.097 kg/kg	0.106 kg/kg
Volum. H_2 stored (V_{st}; 80 K, 50 bar)	0.034 kg/liter	0.043 kg/liter	0.040 kg/liter
Density ratio, V_{st}/ρ_{gas} (80 K, 50 bar)	2.2	2.7	2.6



$$G_{st}(p,T) = G_{ex}(p,T) + [\rho_{gas}(p,T)/\rho_{skel}]\phi/(1-\phi),$$

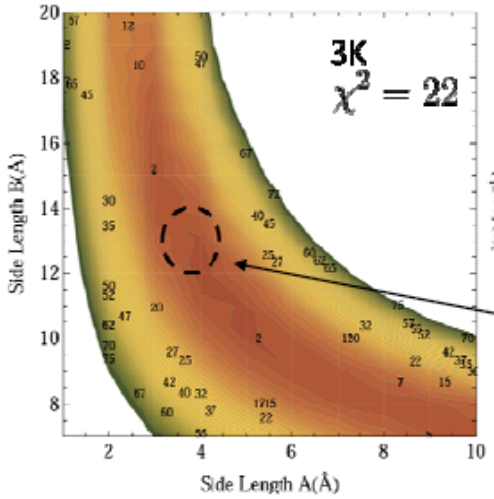
$$V_{st}(p,T) = G_{ex}(p,T)(1-\phi)\rho_{skel} + \phi\rho_{gas}(p,T),$$

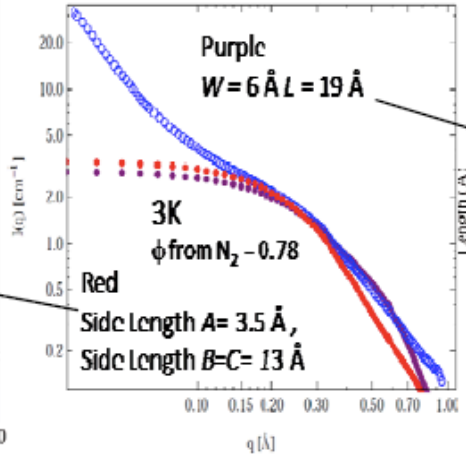
$$V_{st} = \rho_{gas}/[1 - (G_{ex} - \rho_{gas}/\rho_{skel})/G_{st}]$$

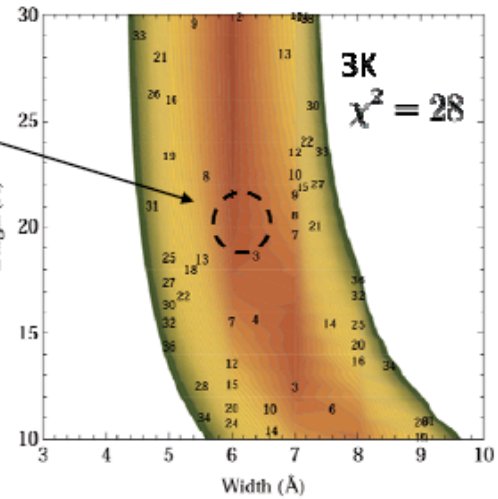
Conclusions:

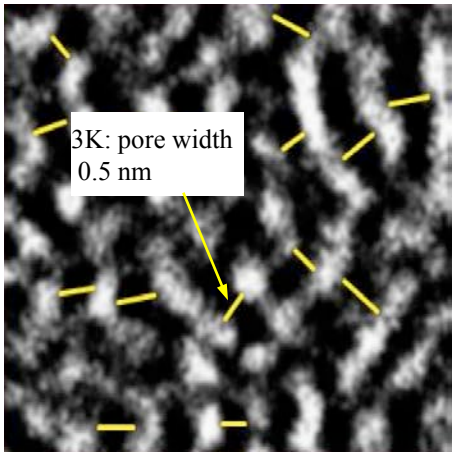
- **Universal relation between V_{st} and G_{st}, parametrized by G_{ex}**
- **Volum. capacity can be increased significantly, with little loss of gravim. capacity, by decreasing the porosity of the adsorbent**

Structural characterization of samples: SAXS & TEM







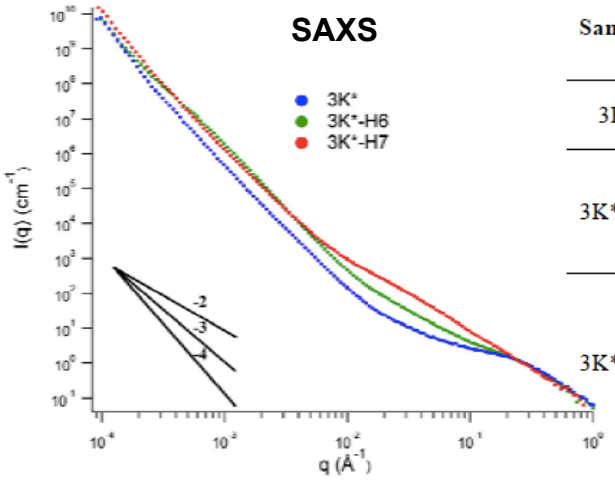


CONCLUSIONS

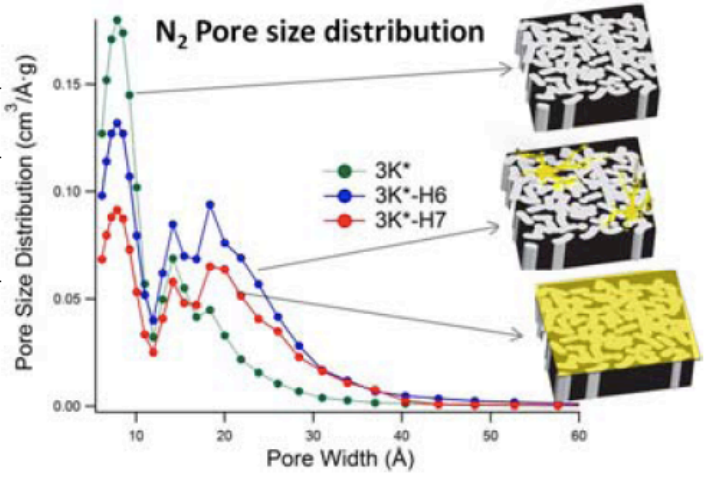
- Morphology from small-angle x-ray scattering (SAXS):
  - Results agree very well with N_2 sorption analysis (pore-size distribution, porosity)
  - Significant departures from “slit-shaped” pores: best fits of 3K and 4K SAXS: *cylindrical pores*
  - (AX-21 is ~slit-shaped)
- Transmission electron microscopy (TEM) of sample 3K consistent with SAXS results
- FY 2010/11: Investigate how different pore structures in our extensive library of carbons correlate with sorption characteristics (particular interest: pore structure of PVDC samples HS;0B and HS;2B).

Structural characterization of samples: SAXS & N_2 adsorption (Aux)

Sample	Porosity from N_2 (ϕ)	N_2 BET surface area (m^2/g)	Cylinder fit (nominal values) (Å)		Box fit (nominal values) (Å)		Gravimetric Excess Adsorption (g/kg)	Total Amount Stored (g/kg)	Gravimetric Excess Adsorption (g/kg)	Total Amount Stored (g/kg)
			Width	Length	Side A	Side B				
3K	0.78	2500	6	19	3.5	13	68.6	97.5	6.6	13.7
4K	0.81	2600	6.5	24	4.4	12	71	106	4.9	12.7
AX-21	0.79	2600	5.5	26	4	12	55.7	90.5	4.7	13.1
3K-H6 Irradiated	0.78	3030	6	24			47.2	75.1	4.3	10.5
							80 K at 50 bar		Room Temp at 50 bar	



Sample	Fabrication method	Boron: Carbon
3K*	3 KOH:C	
3K*-H6	3 KOH:C $B_{10}H_{14}$ deposited as thin liquid film followed by thermal decomposition of $B_{10}H_{14}/B_{10x}H_z$	1.6% weight
3K*-H7	3 KOH:C Submonolayer of $B_{10x}H_z$ is created by thermal decomposition of $B_{10}H_{14}$ liquid/vapor followed by thermal decomposition of $B_{10x}H_z$	6.9% weight



CONCLUSIONS

- SAXS: pore size *and shape*.
- SAXS: fractal analysis indicates formation of dendrites (B:C = 1.6%) and quasi-2D film (B:C = 6.9%).
- SAXS: insight how to improve H_2 sorption characteristics of activated carbons doped via $B_{10}H_{14}$.

This slide serves as supporting data for previous slide

Collaborations

- **Midwest Research Institute** (Private Sector): Subcontractor for design and construction of test vessel for monoliths, under conditions comparable to a full-fledged hydrogen tank.
- **NREL** (Federal): Validation of H_2 uptake data. [L. Simpson, P. Parilla, K. O'Neill]
- **Advanced Photon Source/ANL** (Federal): Ultra-small-angle x-ray scattering studies of samples under General User Program (GUP-10069, GUP-20661). [J. Ilavsky]
- **NIST** (Federal): Collaboration with Y. Liu and G. Brown 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 to obtain adsorption potentials for H_2 sorption on B-substituted materials from ab initio quantum-chemical computations.

Future Work: Plans for 2010/11

- Etch fission tracks in irradiated materials. Compare performance of etched/non-etched materials. Continue investigation whether H_2 and N_2 see same surface area, and of irradiation-induced increase in binding energy.
- Investigate pressure/temperature/pore-shape dependence of new variable ρ_{film} (T) (density of saturated film, "footprint" of H_2 molecule) experimentally and by GCMC simulations. Design materials with high ρ_{film} (T), as concurrent strategy with raising the binding energy
- Improve theoretical models for analysis of excess adsorption isotherms (p_{max}, p_0, $\partial G_{ex}/\partial p$) in terms of E_B (multiple binding energies) and Σ_{H2}. Test for temperature independence of E_B and Σ_{H2}.
- Compare E_B's from p_{max}, from experimental isosteric heats, and from GCMC simulations of isosteric heats, at 80 K and 300 K. Compare E_B's at 80 K and 300 K (should be same).
- Develop understanding of relation between H_2 storage at 80 K and 300 K.
- Expand experimental library of high E_B's from B-doping. Investigate performance of materials without exposure to air, as a function B concentration and thermal annealing. Extend QC calculations of, and GCMC simulations on, B-doped materials to higher B concentrations. Develop theoretical estimates of H_2-wall vibrational frequencies on B-doped materials.
- Attempt synthesis of bulk BC_3 and test for predicted H_2 intercalation (Cooper et al.)
- Manufacture monoliths and design test vessel for monoliths.

Project Summary

- Manufactured B-substituted carbon by thermolysis of $B_{10}H_{14}$, with B:C = 1-7 wt% and without compromising high surface areas.
- Demonstrated that B-substitution raises average binding energy to 9-11 kJ/mol (B:C = 1.4 wt%) and alters entire shape of adsorption isotherm (B:C = 1.7 wt%), consistent with theory. Ab initio calculations of H_2-(B,C) interactions and GCMC simulations gave E_B = 10-14 kJ/mol and gravimetric storage capacities of ~5 wt% at B:C = 10 wt%, 300 K, and 100 bar.
- Developed method to determine isosteric heats of adsorption at *all* coverages.
- Computational work helped understand unexpected variety of adsorption on materials.
- Found unexpected variations of saturated-film densities at 80 K. Resulted in increases of areal excess adsorption, more than twice the "Chahine value" of 20 μg/m^2 at 77 K and 50 bar.
- Observed "pore drilling" by fission products from boron neutron capture. Irradiation significantly changed H_2 adsorption: increased binding energy and decreased film density.
- Developed universal relation between volumetric and gravimetric storage capacity, parametrized by gravimetric excess adsorption.
- Best performing materials in project so far:

Material	Surface area (m^2/g)	Gravimetric excess ads.; 80 K, 50 bar (kg/kg)	Gravimetric storage cap.; 80 K, 50 bar (kg/kg)	Areal excess ads.; 80 K, 50 bar (μg/m^2)	Gravimetric excess ads.; 303 K, 100 bar (kg/kg)	Gravimetric storage cap.; 303 K, 100 bar (kg/kg)	B:C (wt%)	Isosteric heat; 85 K, H_2:C = 0.5 wt%, ~2 bar (kJ/mol)
MSC-30	2600	0.056	0.086	21	0.0073	0.022	0	5.4
3K (6/08)	2500	0.069	0.091	27	0.011	0.023	0	6.7
4K (6/08)	2600	0.071	0.106	27	0.0048	0.020	0	6.1
3K-H6 (II,A)	3300	0.049	0.076	15	0.0065	0.018	1.4	7.5
HS;0B	700	0.034	0.040	47	0.013	0.015	0	TBD