Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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2009 DOE Annual Merit Review, May 18-22, 2009, Arlington, VA

Project ID #ST_31_Pfeifer

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Overview

Timeline

- Project start date: September 1, 2008
- Project end date: January 31, 2012
- Percent complete: 10%

Budget

- Total project funding:
  - DOE share: $1.90M
  - Contractor share: $0.51M
- Funding FY08-09:
  - DOE share: $579K
  - Contractor share: $166K

Barriers

Barriers addressed:

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

Partners

Interactions/collaborations:

- 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
- S. Kjelstrup—Norwegian U. Science & Technology, Trondheim

Objectives

Overall:

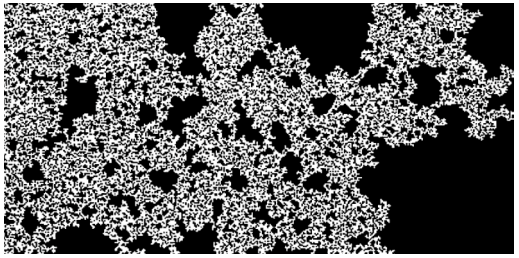
- Fabricate high-surface-area, multiply surface-functionalized nanoporous carbon (B, Fe, Pt, …), derived from corncob, for reversible H_2 storage with superior storage capacity:
  1) Create surface areas ≥ 4500 m^2/g and average binding energy ≥ 12 kJ/mol
  2) Fabricate non-hybrid materials, functionalized with B, Fe, …, but not Pt: physisorption of H_2 on high-surface-area, high-binding-energy surfaces
  3) Fabricate hybrid materials, functionalized with B, Fe, … and Pt with spillover capability: physisorption of H_2 & chemisorption of H on one and the same surface
- Characterize materials & demonstrate storage performance
  1) Determine pore-space architecture, structure of B, Fe, Pt, … sites/clusters, associated sorption H_2 isotherms (1-100 bar), isosteric heats, and kinetics, at 77-450 K
  2) Validate theoretical modeling predictions (computer simulations of binding energies, sorption isotherms, surface diffusion)
- Optimize pore architecture and composition
  1) Use computer simulations as function of surface architecture & composition, to provide directions for optimization
  2) Fabricate monoliths of optimized materials; determine storage capacities and charge/discharge kinetics under conditions comparable to an on-board H_2 tank
  3) Reach target of 60 g H_2/kg carbon and 45 g H_2/liter carbon at 50 bar and 300 K, on non-hybrid monoliths, with pressure swing alone
  4) Reach target of 90 g H_2/kg carbon and 81 g H_2/liter carbon either (a) at 50 bar and 100 K, on non-hybrid monoliths, with pressure swing alone; or (b) at 50 bar and 300 K, on hybrid monoliths, with combined pressure and temperature swing

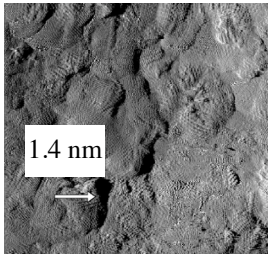
Approach

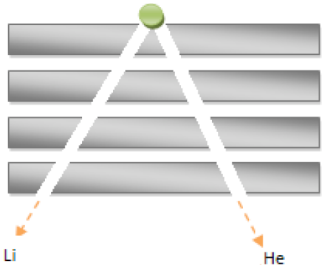
- Maximize surface area
  Maximizes # of adsorption sites
  ('Engineered Nanospaces I')
  - High-surface area carbon from corncob (U. Missouri patent pending): S_i ~ 3000 m^2/g
  - Substitute with B and create additional surface area by boron neutron capture, fission into Li and alpha particle,

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

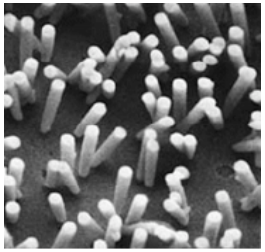
    (U. Missouri Research Reactor), and etching of fission tracks
  - U. Missouri (2009):
    Theor. optimum track width: w ~ 1 nm
    Theor. max. surface area: $S_f = 2S_i$

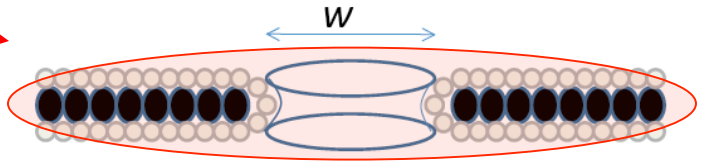




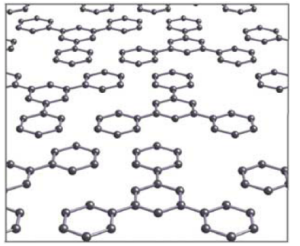


Nucleopore (track-etched poly-carbonate membrane)

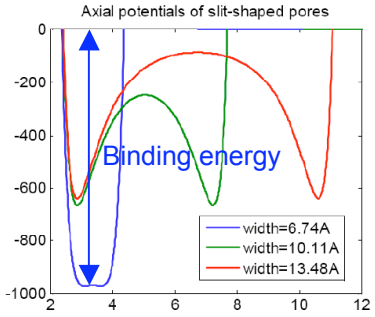


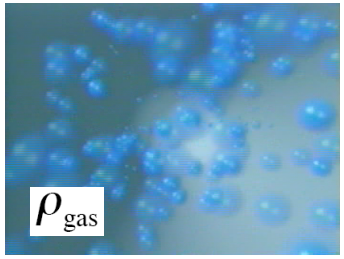


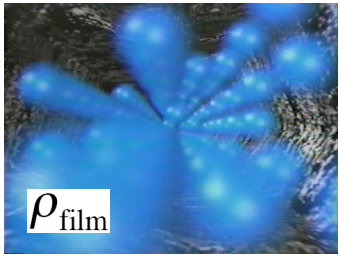
Excision of six-membered rings gives 6200 m^2/g (Chae *et al.*, 2004)



- 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: $\rho_{film,\ narrow\ pore} >> \rho_{film,\ wide\ pore} >> \rho_{gas}$

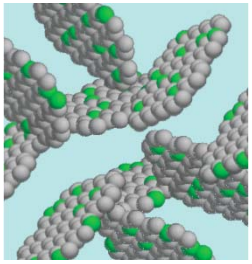


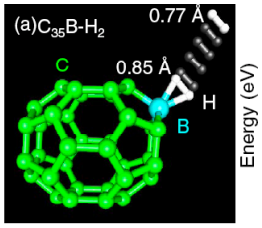




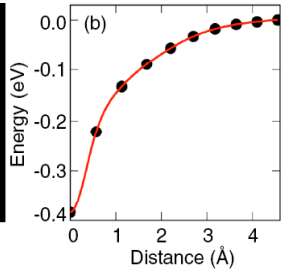
Approach, Cont.'d

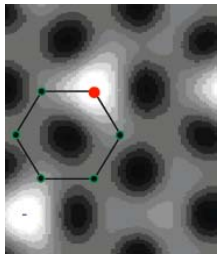
- Surface functionalization with B/Fe/… ('Substituted Materials')
  Raises H_2 binding energy further
  – Substitute with boron:
  Binding energy of H_2 on graphite: 5 kJ/mol
  Binding energy of H_2 on B-substituted carbon: 10-30 kJ/mol
  (electron donation from H_2 to electron-deficient B)
  Twofold use of B: (a) boron neutron capture;
  (b) remaining B increases binding energy
  – Substitute with Fe:
  Fe atoms/clusters increase binding energy (mechanism yet to be understood)
  – Perform atomistic computer simulations of H_2 sorption to determine optimal pore architecture and B/Fe/… conc.

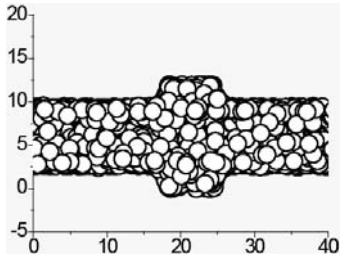




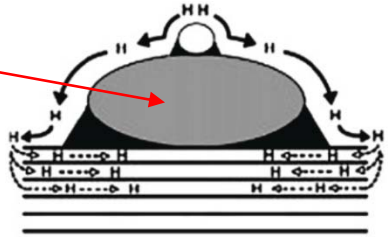
Kim *et al.*, 2006



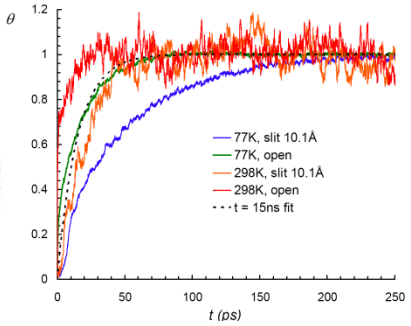




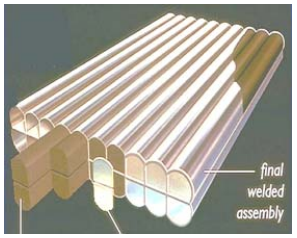
- Surface functionalization with Pt clusters ('Spillover Materials')
  Dissociates H_2 and creates chemisorbed H
  – Binding energy of H on carbon: 20-60 kJ/mol
  – Twofold use of high surface area: (a) physisorbed H_2;
  (b) chemisorbed H.
  – Perform computer simulations of H surface diffusion and ads./des. kinetics to determine optimal Pt distribution



Lachawiec *et al.*, 2005



- 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



Materials synthesis and performance

Measures of H_2 adsorption of interest

Adsorbed film & non-adsorbed gas in pore.

Sample mass: m_s

Specific surface area: Σ

Porosity: ϕ

Skeletal density of sample: ρ_{skel}

Apparent density of sample (incl. pore space): ρ_{app}

Excess mass adsorbed, $m^e_{ads}(p,T)$

Mass of adsorbed H_2, less mass of equal volume of H_2 in the absence of adsorption

Total mass stored, $m_{st}(p,T)$

Mass of adsorbed & non-adsorbed H_2

- Gravimetric excess adsorption: $\dfrac{m^e_{ads}(p,T)}{m_s}$

  Direct experimental quantity; depends only on Σ and how strongly surface adsorbs H_2, but not on pore volume

- Areal excess adsorption (Liu *et al.*, 2008): $\dfrac{m^e_{ads}(p,T)}{m_s \Sigma}$

  Depends only on how strongly surface adsorbs H_2
  Is (p,T)-dependent measure of binding energy

- Gravimetric storage capacity:

$$\frac{m_{st}(p,T)}{m_s} = \frac{m^e_{ads}(p,T)}{m_s} + \frac{\rho_{gas}(p,T)}{\rho_{skel}} \frac{\phi}{1-\phi}$$

  Increases with increasing porosity

- Volumetric storage capacity:

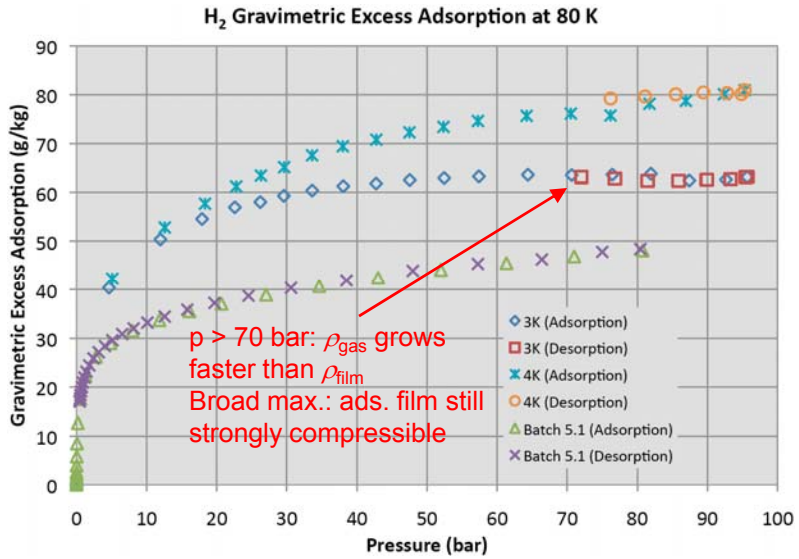
$$\frac{m_{st}(p,T)}{m_s}\rho_{app} = \left[\frac{m^e_{ads}(p,T)}{m_s}\rho_{skel} - \rho_{gas}(p,T)\right](1-\phi) + \rho_{gas}(p,T)$$

  Increases with decreasing porosity

Independent design variables

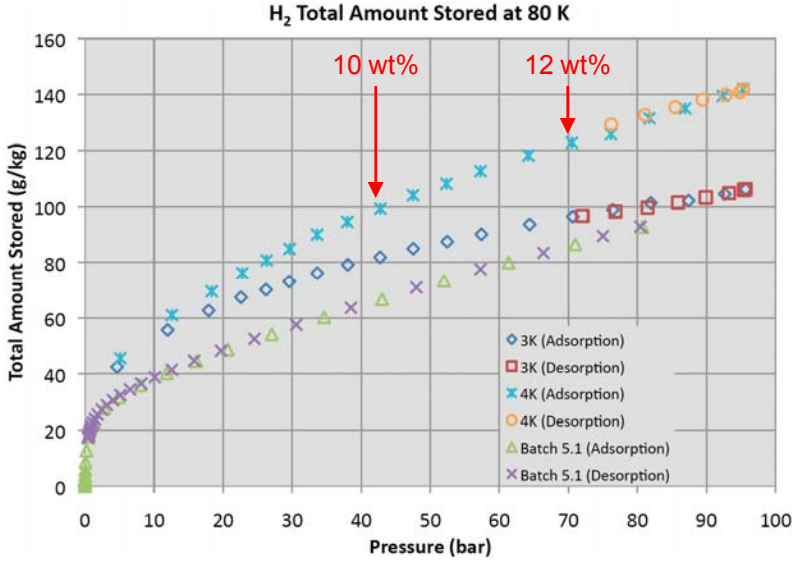
- In present case studies:
  – Σ from BET analysis of N_2 adsorption isotherm at 77 K, $0.01 \le p/p_0 \le 0.03$, rounded to nearest hundred
  – ϕ from N_2 adsorption at 77 K, at $p/p_0 = 0.995$
  – H_2 sorption excess isotherms measured volumetrically on Hiden HTP sorption analyzer

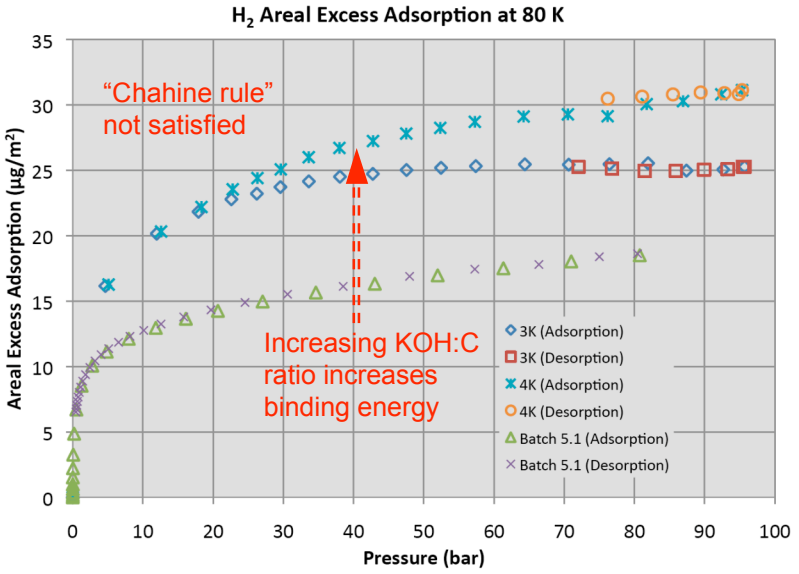
Materials synthesis and performance: boron-free carbons



Precursors for B-substitution

	Batch 5.1	3K	4K
Ratio KOH:C for chem. activation	2:1	3:1	4:1
Specific surface area (Σ)	2600 m^2/g	2500 m^2/g	2600 m^2/g
Porosity (ϕ)	0.77	0.75	0.81
"Chahine rule" (1 wt% exc. H_2 per 500 m^2/g @ 77 K & 40 bar) predicts	~5 wt%	~5 wt%	~5 wt%
Gravim. excess H_2/C @ 50 bar	4.4 wt%	6.3 wt%	7.3 wt%
Gravim. stored H_2/C @ 50 bar	7.3 wt%	8.6 wt%	10.6 wt%
Volum. stored H_2/C @ 50 bar	34 g/liter	43 g/liter	40 g/liter

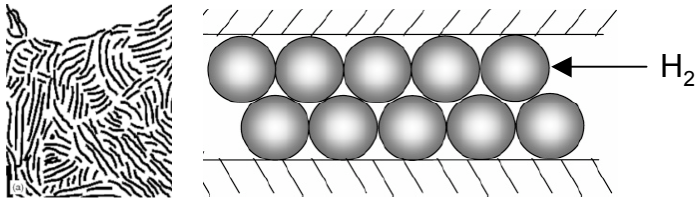




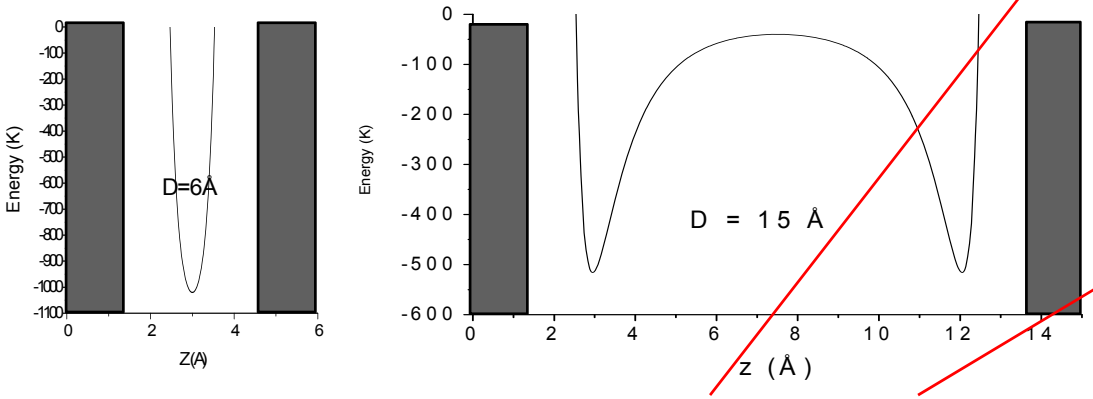
Materials synthesis and performance: boron-free carbons, cont.'d

Departures from "Chahine rule" due to high binding energies, E_B ~ 9 kJ/mol, in narrow pores

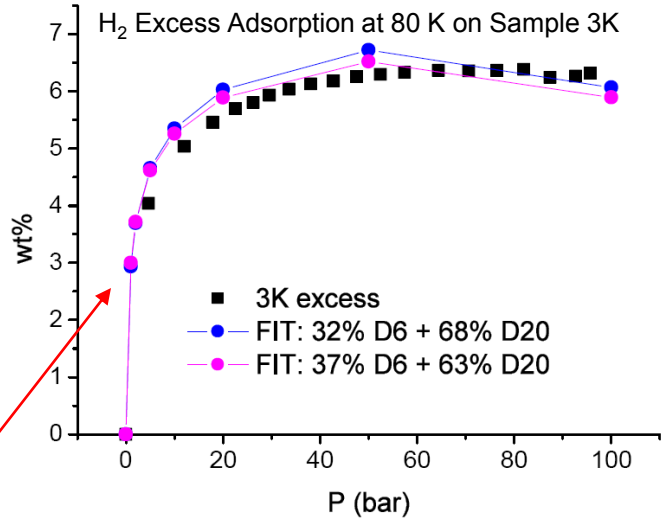
- Preparation of carbons suggests approximately slit-shaped pores reminiscent of exfoliated graphite
- Predominant pore width: 0.7-1.2 nm (see materials characterization)

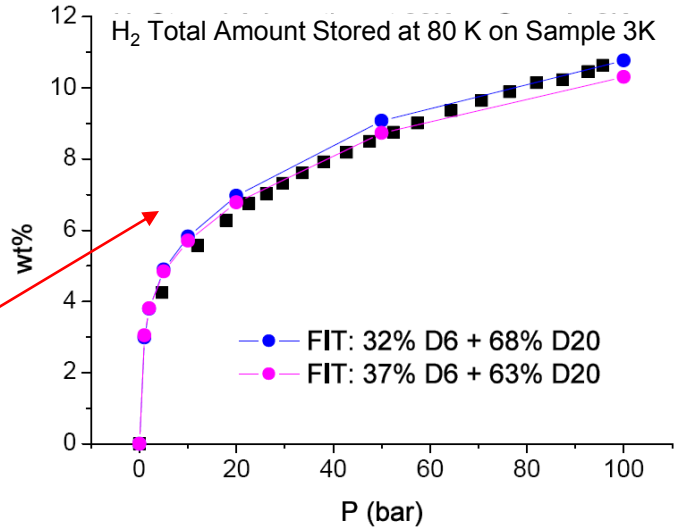


- Grand-canonical Monte Carlo (GCMC) simulations of H_2 adsorption in slit-shaped pores of width 0.6 nm (E_B = 9.0 kJ/mol) and 2.0 nm (E_B = 4.5 kJ/mol), with Σ = 2600 m^2/g (Kuchta & Firlej):



- Best fit to experimental data for Sample 3K (excess ads. & total amt. stored) yields: ~37% sites with E_B = 9.0 kJ/mol; ~63% sites with E_B = 4.5 kJ/mol





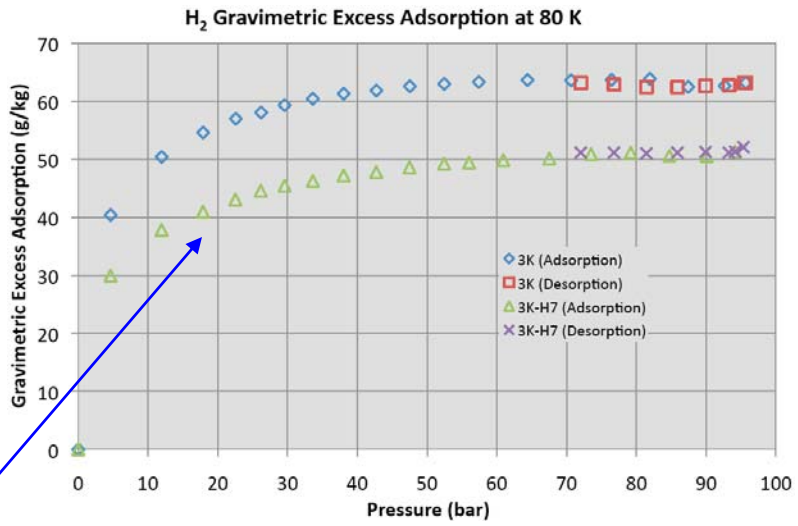
Materials synthesis and performance: boron-substituted carbons

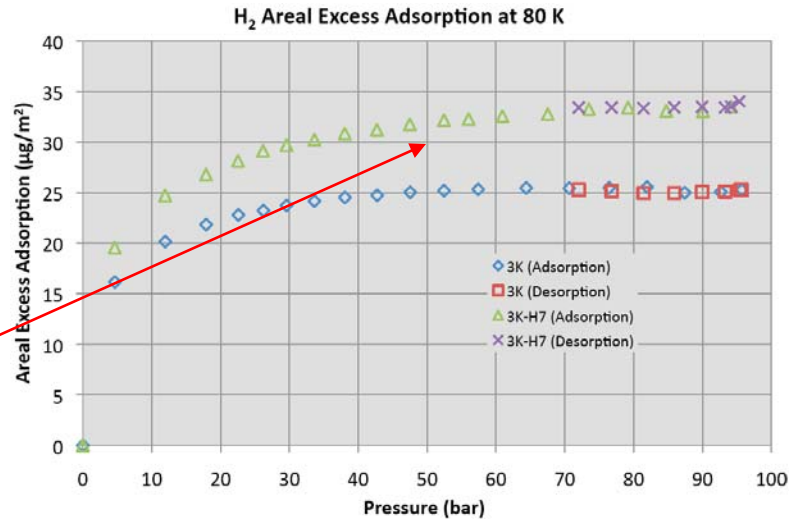
Boron substitution by deposition/decomposition of decaborane ($B_{10}H_{14}$)

- Method I: Deposition of $B_{10}H_{14}$ as thin liquid film; thermal decomposition of $B_{10}H_{14}/B_{10x}H_z$
- Method II: Submonolayer of $B_{10x}H_z$ from thermal decomposition of $B_{10}H_{14}$ vapor (admixed $B_{10}H_{14}$); thermal decomposition of $B_{10x}H_z$
- Method III: Submonolayer of $B_{10x}H_z$ from thermal decomposition of $B_{10}H_{14}$ vapor (sublimed $B_{10}H_{14}$); thermal decomposition of $B_{10x}H_z$
- Representative results:

Reaction	B:C, input	B:C, product (PGAA)	Specific surface area
"3K" (boron-free precursor)	0.0 wt%	0.0 wt%	2500 m^2/g
"3K" + $B_{10}H_{14}$ —Method I→ "3K-H7"	8.8 wt%	6.0 wt%	1500 m^2/g
"3K" + $B_{10}H_{14}$ —Method II→ "3K-H6"	1.8 wt%	1.4 wt%	2400 m^2/g
"3K" + $B_{10}H_{14}$ —Method III→ "3K-H5"	N/A	0.8 wt%	2800 m^2/g

- Case study 3K-H7: gravimetric excess ads. lower than in precursor because surf. area is lower (pore blocking); but areal excess ads. at 50 bar is ~30% higher than in boron-free carbon. Work underway to improve incorporation of B in carbon matrix.

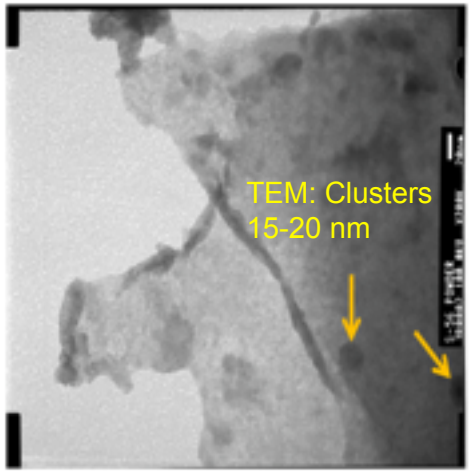




Materials synthesis and performance: magnetic carbons

Magnetic properties of samples

- Bulk graphite with perfect structure is diamagnetic
- Carbon samples activated with KOH in stainless steel reactor are superparamagnetic/ferromagnetic. Suspected origin: Fe clusters in carbon



- Elemental composition of Sample 3K

Element	Sample (PIXE)	Stainless Steel, Grade 340
Cr	990 ppm	17-20%
Mn	130 ppm	<2%
Fe	0.43%	>50%
Ni	190 ppm	8-11%

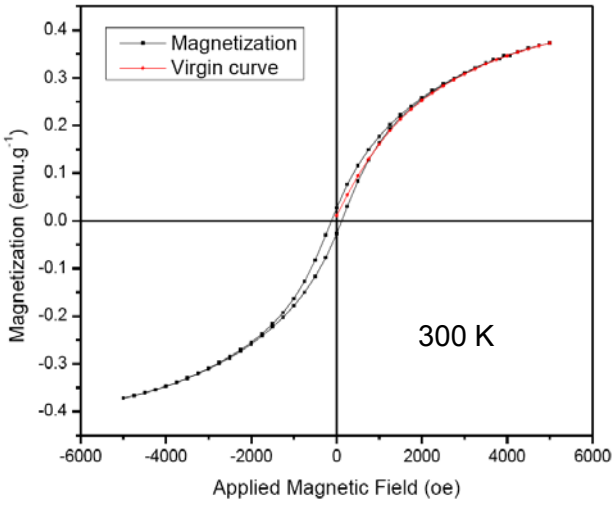
Corncob

Char before KOH treatment

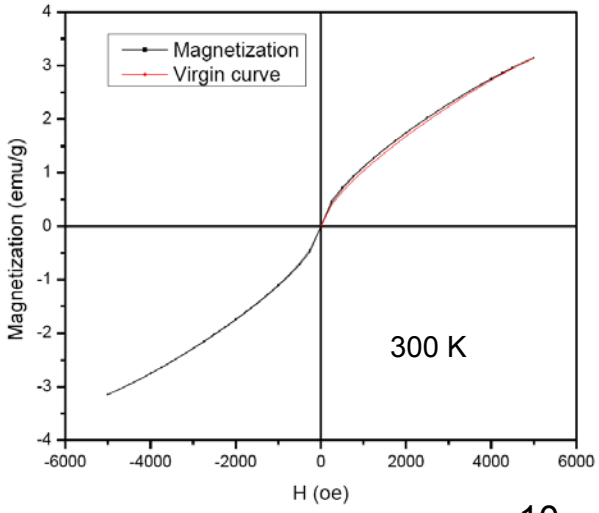
Carbon (3K) after KOH treatment in steel reactor

Carbon (3K*) after KOH treatment in Al_2O_3 reactor

Sample S-33/k is ferromagnetic at 300 K (nonzero coercive field):



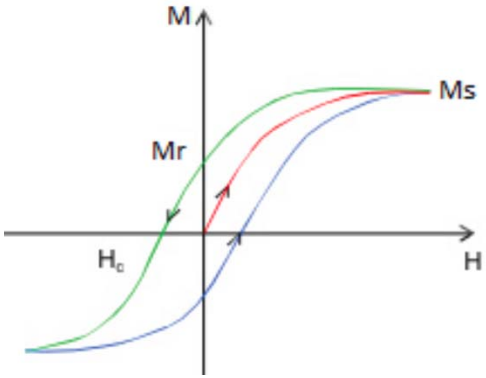
Sample Batch 5.32 is super-paramagnetic at 300 K (zero coercive field):



Materials synthesis and performance: magnetic carbons, cont.'d

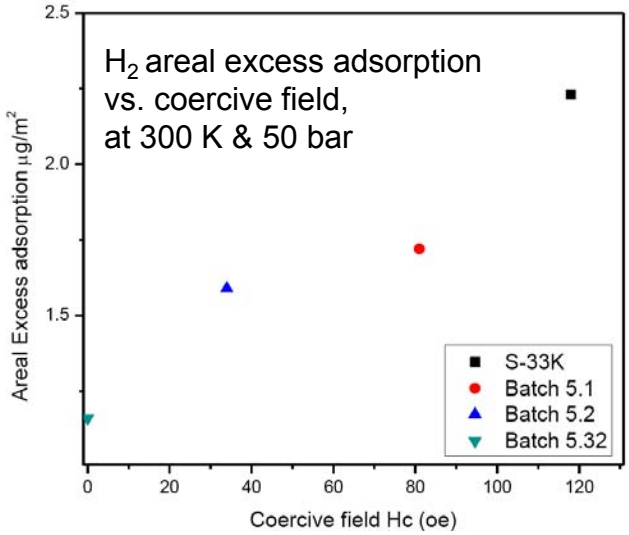
Magnetic properties of samples enhance H_2 adsorption (preliminary results)

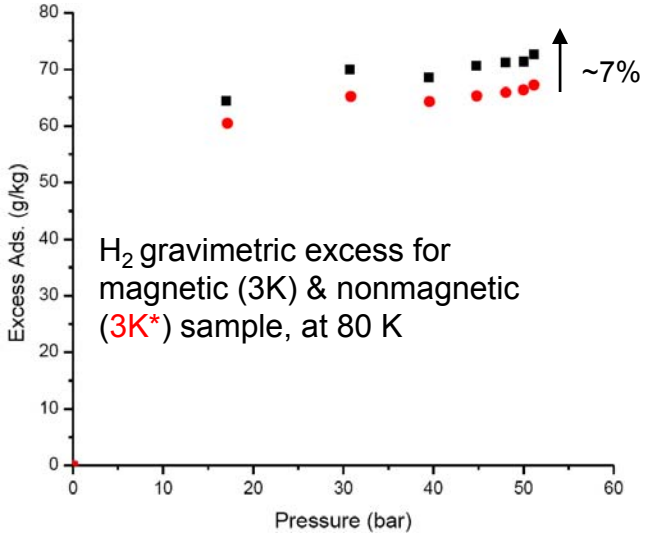
- Saturation magnetization, M_s, remnant magnetization, M_r, coercive field, H_c, and magnetic susceptibility, χ, at 300 K:

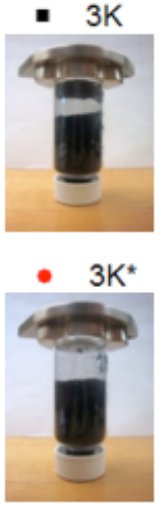


Sample	M_s (emu/g)	H_c (oe)	M_r (emu/g)	χ (emu/g·oe)
S-33/k	0.5	118	$2.69\cdot10^{-2}$	$2.12\cdot10^{-4}$
Batch 5.1	1.3	81.5	$5.05\cdot10^{-2}$	$5.82\cdot10^{-4}$
Batch 5.2	1.5	34	$4.35\cdot10^{-2}$	$1.30\cdot10^{-3}$
Batch 5.32	3.5	$3.1\cdot10^{-5}$	$4.64\cdot10^{-3}$	$1.82\cdot10^{-3}$
Batch 5.4	8	71	$3.37\cdot10^{-1}$	$4.26\cdot10^{-3}$
Darko 2.25	4	68	$5.25\cdot10^{-1}$	$5.65\cdot10^{-3}$

- Measured saturation magnetizations are consistent with Fe-induced magnetism: 0.5 wt% Fe in sample contributes 1.0 emu/g for Fe, and 0.7 emu/g for Fe_3O_4
- Larger coercive fields suggest larger size of magnetic clusters. S-33/k has largest coercive field at 300 K.

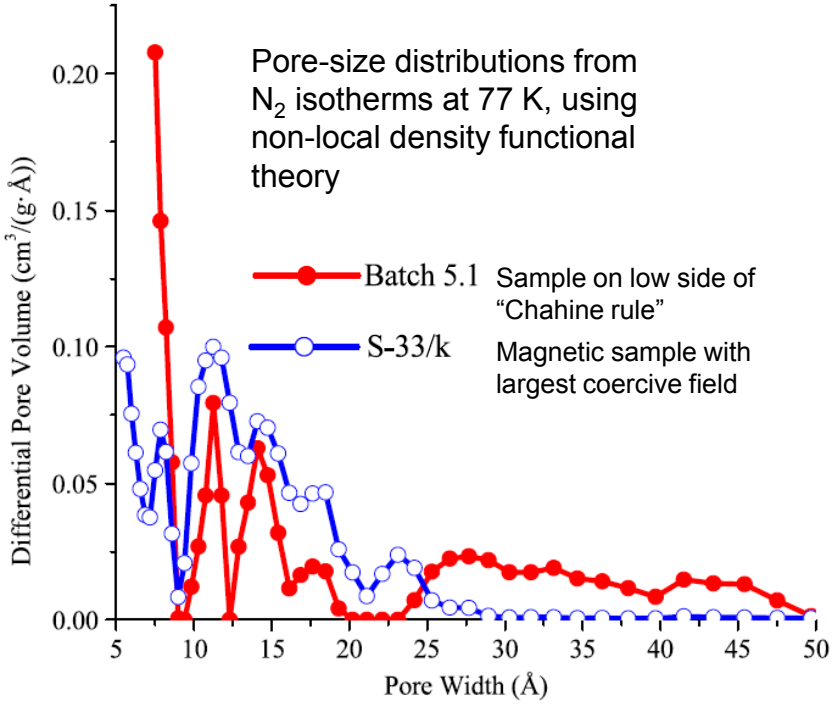


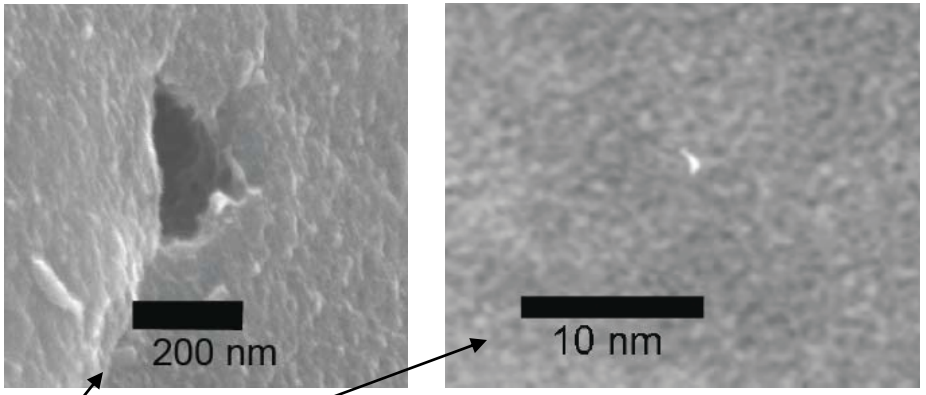




Structural characterization of samples

Surface/pore structure of selected samples





SEM and TEM of S-33/k confirm essential absence of large pores

- Significant presence of pores larger than 1.0 nm in Batch 5.1 is consistent with its underperformance relative to "Chahine rule"
- Burress *et al.*, *Nanotechnology* **20** (2009):
  Batch 5.1: ~25% high-binding-energy sites for H_2
  S-33/k: ~40% high-binding-energy sites for H_2,
  consistent with its high H_2 areal excess adsorption as a function of coercive field

MD simulations in pores of variable width predict two distinct binding energies:

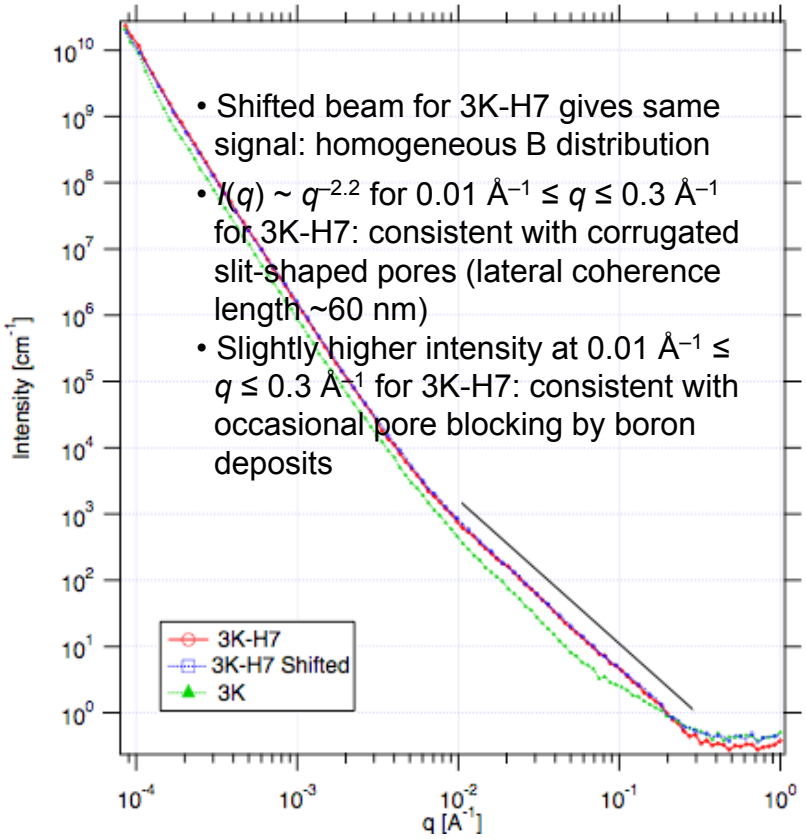
	Low energy (width ≥ 1.0 nm)	High energy (width <1.0 nm)
Prediction:	~5 kJ/mol	~8 kJ/mol
Exp./Batch 5.1:	4.8 kJ/mol	9.0 kJ/mol
Exp./S-33/k:	6.4 kJ/mol	8.6 kJ/mol

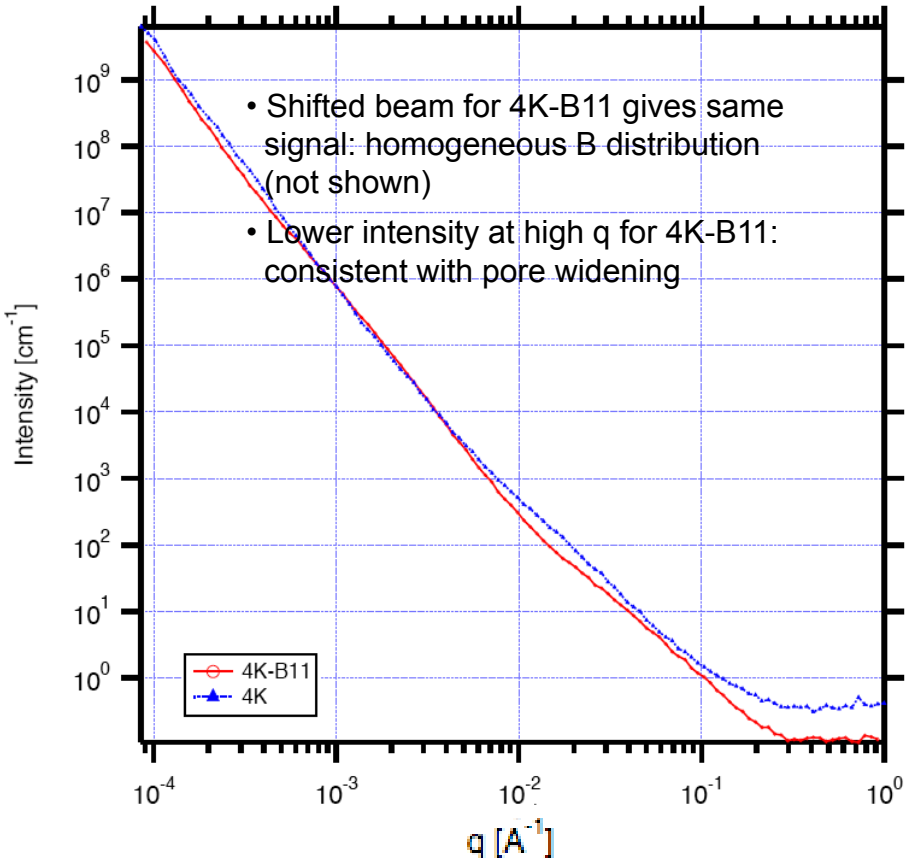
Structural characterization of samples, cont.'d

Ultra-small-angle x-ray scattering (Advanced Photon Source) from B-free and B-substituted carbons

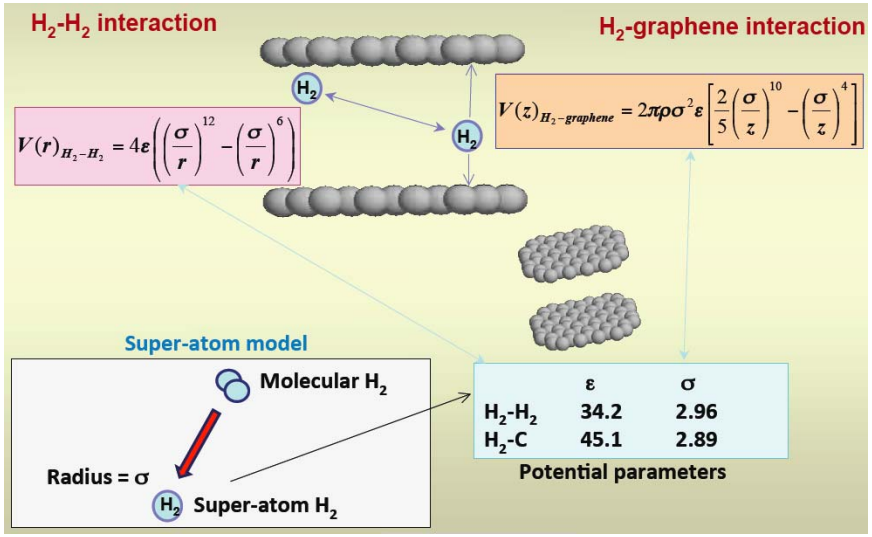
Sample 3K: B-free carbon, KOH activation; 2500 m^2/g
Sample 3K-H7: thermolysis of $B_{10}H_{14}$ on 3K; 6 wt% B (PGAA); 1500 m^2/g

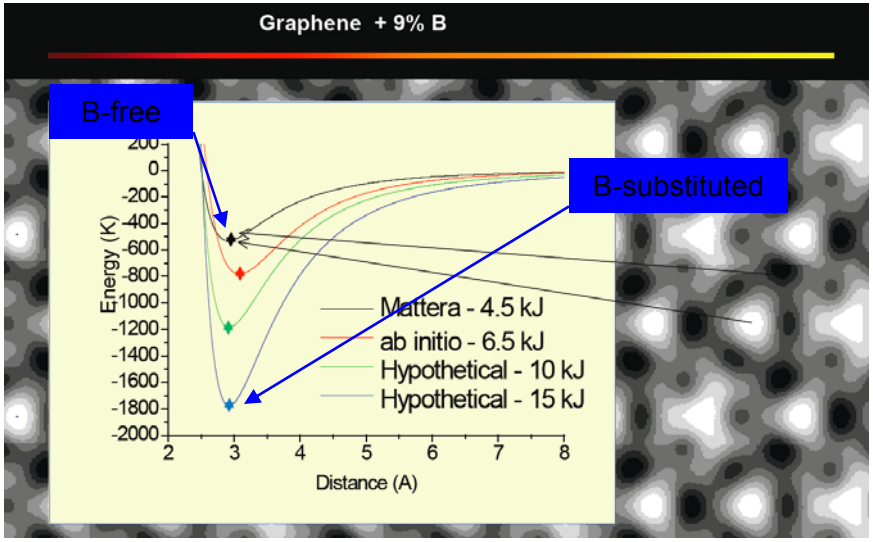
Sample 4K: B-free carbon, KOH activation; 2600 m^2/g
Sample 4K-B11: B-substituted carbon, KOH/KBH_4 activation; 7 wt% B (PGAA); surface area TBD

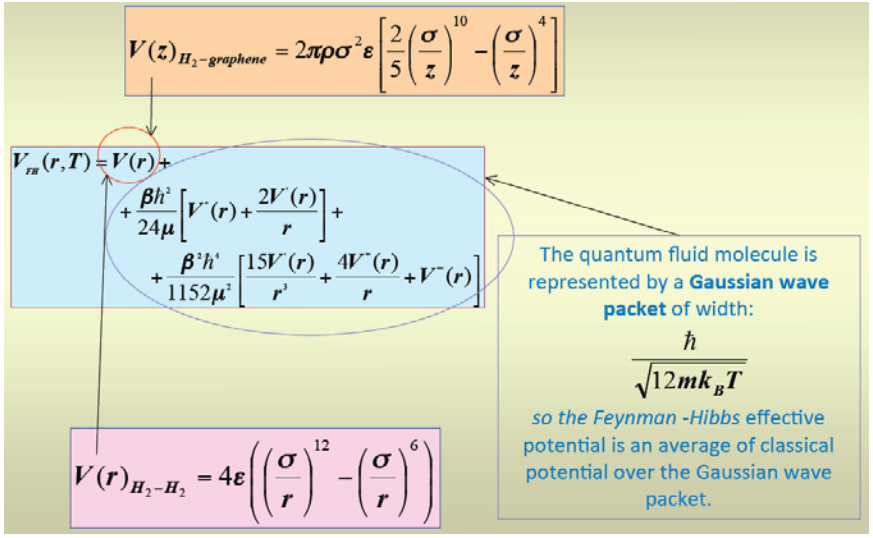


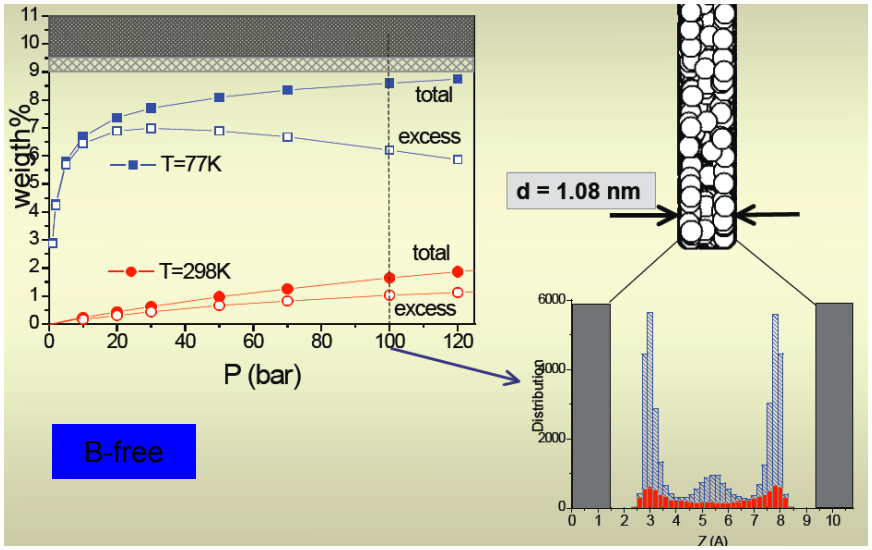


GCMC simulations in B-substituted materials

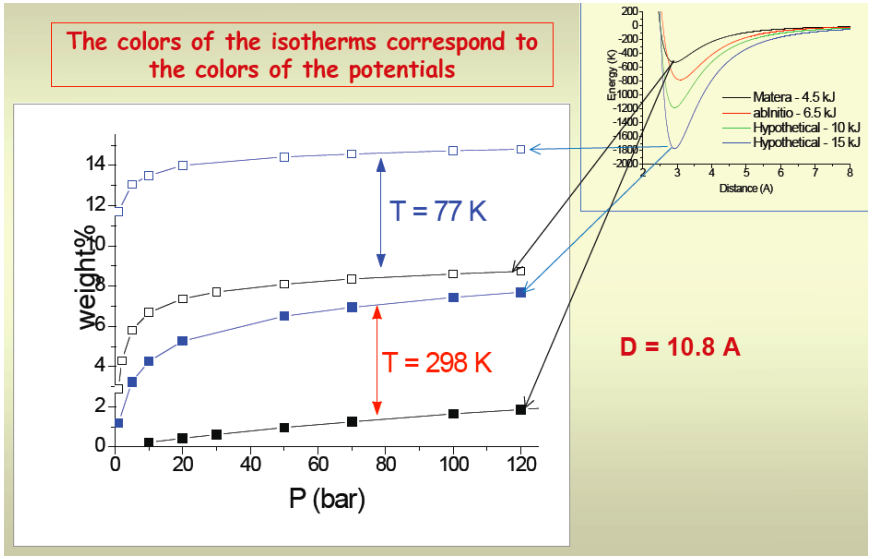


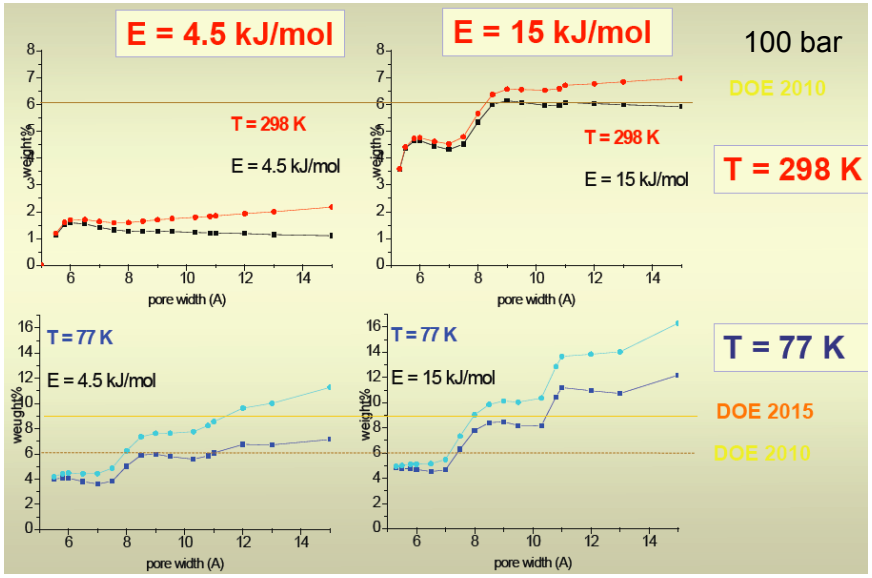


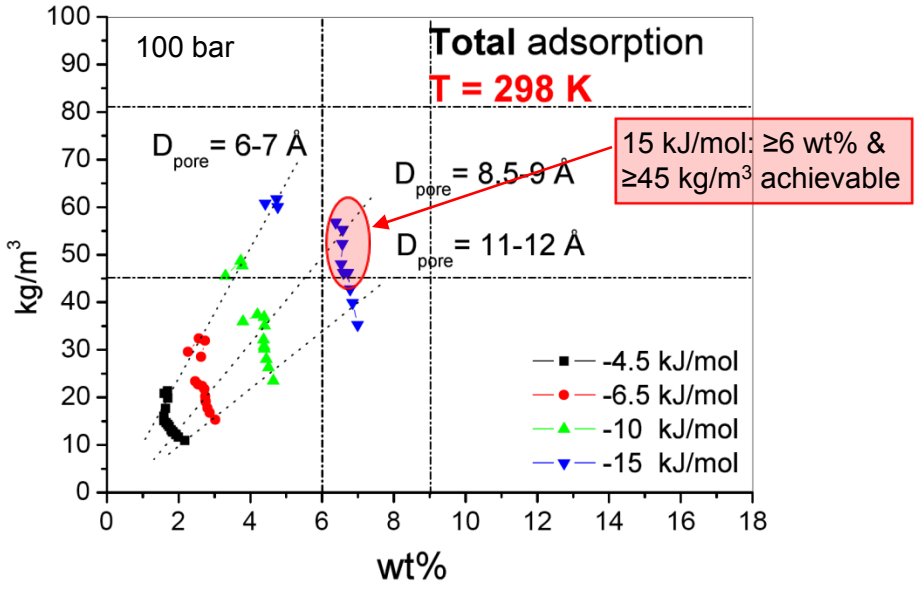


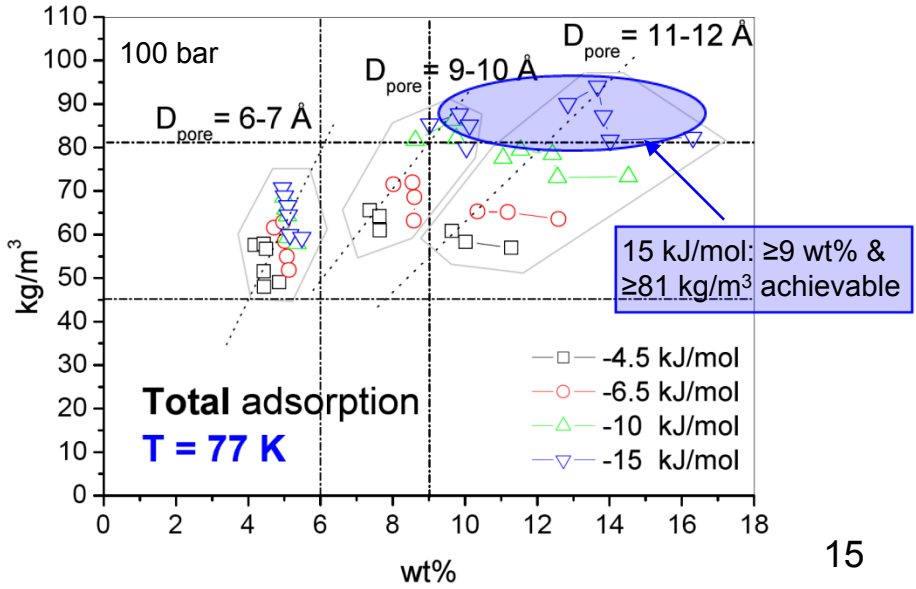


GCMC simulations in B-substituted materials, cont.'d









Conclusions

- For given gravimetric excess adsorption (independent of pore volume), gravimetric and volumetric *storage capacity* can be engineered by appropriate choice of porosity (independent design variable).
- Manufactured boron-free carbon with gravimetric excess adsorption of >7 wt%, gravimetric storage capacity of >10 wt%, and volumetric storage capacity of 40 g/liter, at 80 K and 50 bar.
- Departures from “Chahine rule” seen. Attributed to high binding energies in narrow pores. Validated by GCMC simulations with binding energy ~9 kJ/mol in narrow pores, present on ~40% of total surface.
- Manufactured boron-substituted carbon by thermolysis of decaborane, with ~30% higher areal excess adsorption at 80 K and 50 bar, from 6 wt% boron. Suggests significant increase in binding energy. Boron-substituted carbons can be made in this way without compromising large surface areas.
- Observed magnetic carbons, with enhanced H_2 adsorption, from ~0.5 wt% Fe.
- Performed GCMC simulations of sorption equilibria on surfaces with 15 kJ/mol binding energy and variable pore width. Attractive H_2-H_2 interactions make pores of width > 1.0 nm have unexpectedly high storage capacities. Simulations predict that >6 wt% and >45 kg/m^3 can be achieved at 298 K &100 bar, and > 9 wt% and >81 kg/m^3 at 77 K & 100 bar, for various pore widths.

Collaborations

- Midwest Research Institute (Private Sector): Subcontractor for design and construction of test vessel for hybrid and nonhybrid monoliths, under conditions comparable to a full-fledged hydrogen tank.
- NREL (Federal): Validation of H_2 uptake data.
- Advanced Photon Source/ANL (Federal): Ultra-small-angle x-ray scattering studies of samples under General User Program (GUP-10069).
- 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 materiasls from ab initio quantum-chemical computations.
- S. Kjelstrup, Norwegian U. Science & Technology, Trondheim (Academic): Collaboration on experimental and computational studies of diffusion of chemisorbed hydrogen on carbon surfaces.

Future Work: Plans for 2009/10

- Investigate performance of boron-substituted materials, including isosteric heats of adsorption, as a function of deposition condition of decaborane; investigate role of thermal annealing.
- Compare results with other methods of introducing boron into carbon matrix.
- Determine chemical nature of boron in substituted materials.
- Perform GCMC simulations of H_2 sorption equilibria on B-substituted materials with adsorption potentials determined from ab initio computations.
- Investigate physical mechanism of enhanced H_2 adsorption on magnetic/Fe-containing materials (interaction of spin isomers of H_2 with magnetic clusters; Fe as catalyst for dissociation of H_2 and s chemisorbed atomic hydrogen).
- Manufacture and investigate performance of materials with spillover capability.
- Create additional surface area by boron neutron capture an etching of fission tracks.