Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

P. Pfeifer[1], C. Wexler[1], G. Suppes[2], F. Hawthorne[1,3,4], S. Jalisatgi[4], M. Lee[4], D. Robertson[3,5]

[1]Dept. of Physics, [2]Dept. of Chemical Engineering, [3]Dept. of Chemistry, [4]Dept. of Radiology, [5]University of Missouri Research Reactor

University of Missouri, Columbia, MO 65211

P. Buckley, J. Clement

Midwest Research Institute, Kansas City, MO 64110

Hydrogen Sorption Center of Excellence

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

Project ID #ST_31_Pfeifer

Alliance for Collaborative Research in Alternative Fuel Technology

Midwest Research Institute

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:

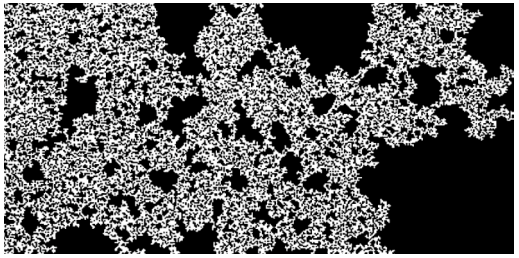
- Fabricate high-surface-area, multiply surface-functionalized nanoporous carbon (B, Fe, Pt, …), derived from corncob, for reversible H_2 storage with superior storage capacity:
  1) Create surface areas ≥ 4500 m^2/g and average binding energy ≥ 12 kJ/mol
  2) Fabricate non-hybrid materials, functionalized 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

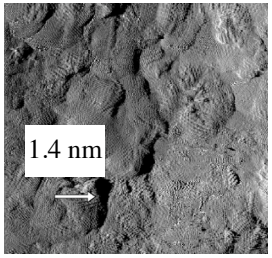
Approach

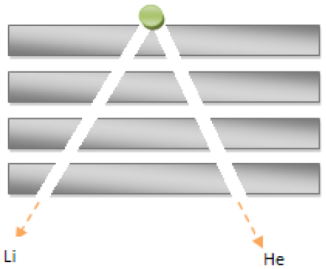
- Maximize surface area
  Maximizes # of adsorption sites
  ('Engineered Nanospaces I')
  - High-surface area carbon from corncob (U. Missouri patent pending): S_i ~ 3000 m^2/g
  - Substitute with B and create additional surface area by boron neutron capture, fission into Li and alpha particle,

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

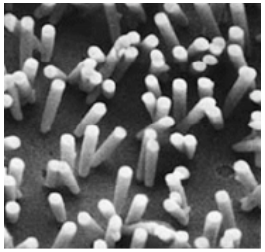
    (U. Missouri Research Reactor), and etching of fission tracks
  - U. Missouri (2009):
    Theor. optimum track width: w ~ 1 nm
    Theor. max. surface area: $S_f = 2S_i$

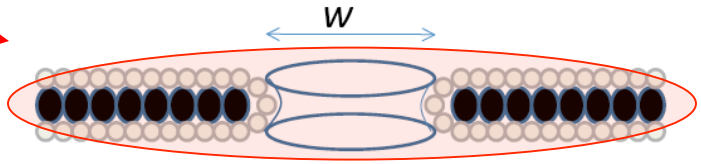




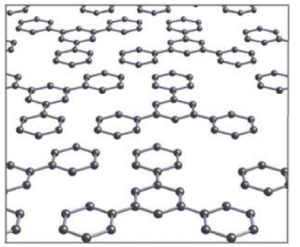


Nucleopore (track-etched poly-carbonate membrane)

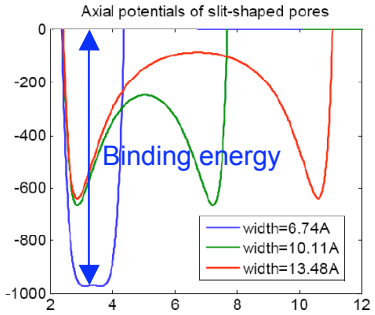


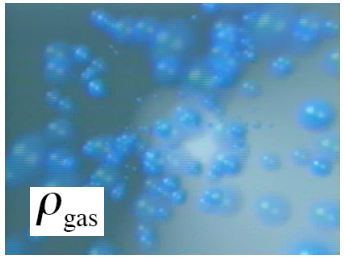


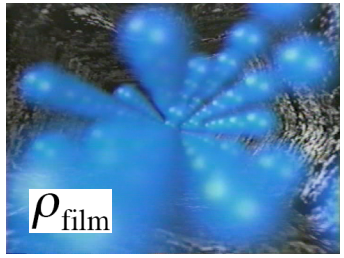
Excision of six-membered rings gives 6200 m^2/g (Chae *et al.*, 2004)



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

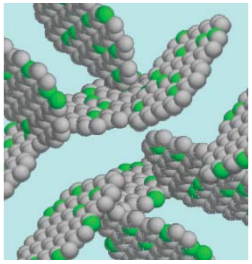


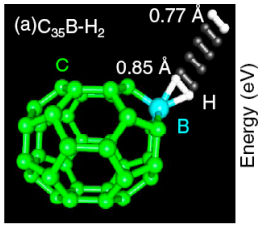




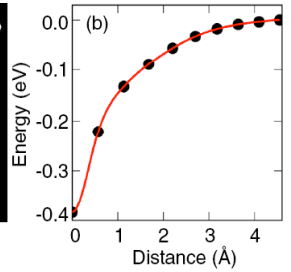
Approach, Cont.'d

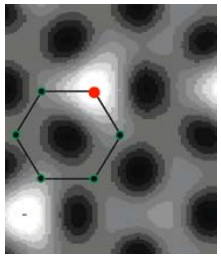
- Surface functionalization with B/Fe/… ('Substituted Materials')
  Raises H_2 binding energy further
  – Substitute with boron:
  Binding energy of H_2 on graphite: 5 kJ/mol
  Binding energy of H_2 on B-substituted carbon: 10-30 kJ/mol
  (electron donation from H_2 to electron-deficient B)
  Twofold 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.

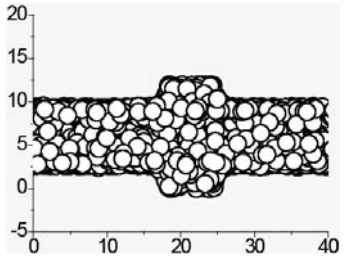




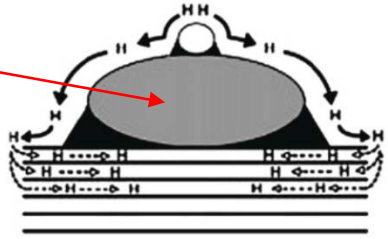
Kim *et al.*, 2006



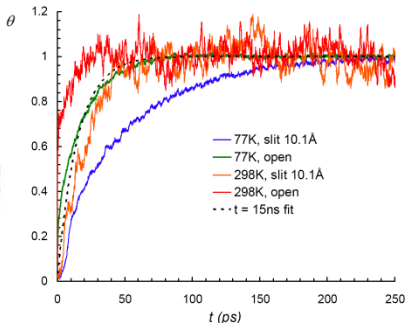




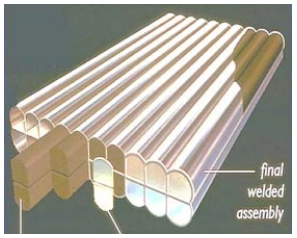
- Surface functionalization with Pt clusters ('Spillover Materials')
  Dissociates H_2 and creates chemisorbed H
  – Binding energy of H on carbon: 20-60 kJ/mol
  – Twofold use of high surface area: (a) physisorbed H_2;
  (b) chemisorbed H.
  – Perform computer simulations of H surface diffusion and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

- Gravimetric excess adsorption: $\frac{m^{e}_{ads}(p,T)}{m_s}$

  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): $\frac{m^{e}_{ads}(p,T)}{m_s \Sigma}$

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

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 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

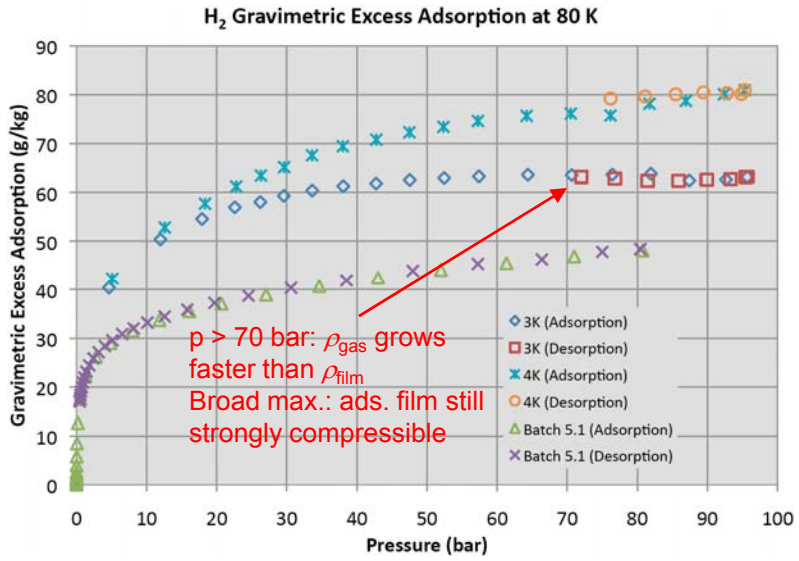
- Volumetric storage capacity: $\frac{m_{st}(p,T)}{m_s}\rho_{app} = \left[\frac{m^{e}_{ads}(p,T)}{m_s}\rho_{skel} - \rho_{gas}(p,T)\right](1-\phi) + \rho_{gas}(p,T)$

  Increases with decreasing porosity

Independent design variables

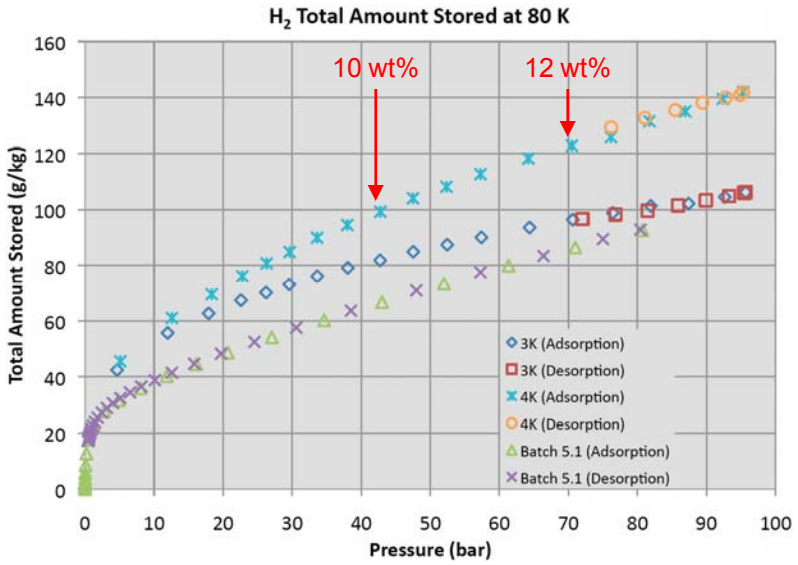
- In present case studies:
  – Σ from BET analysis of N_2 adsorption isotherm at 77 K, $0.01 \le p/p_0 \le 0.03$, rounded to nearest hundred
  – ϕ from N_2 adsorption at 77 K, at $p/p_0 = 0.995$
  – H_2 sorption excess isotherms measured volumetrically on Hiden HTP sorption analyzer

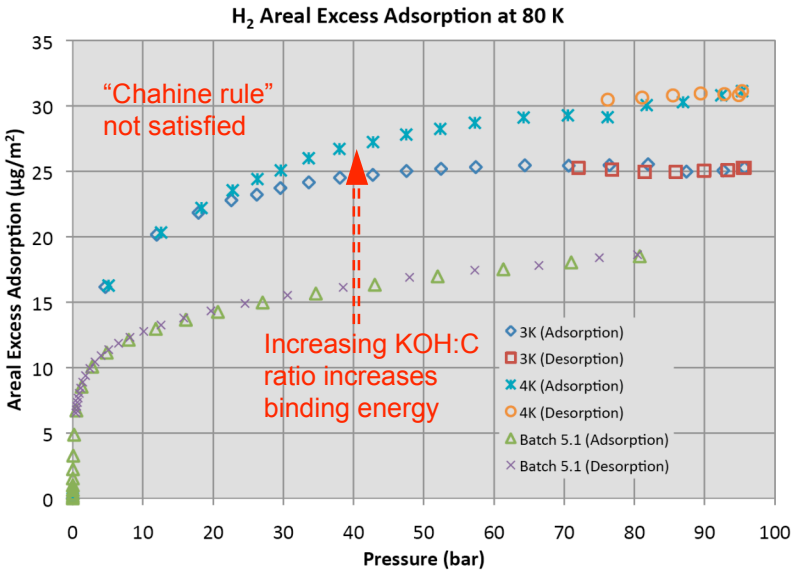
Materials synthesis and performance: boron-free carbons



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

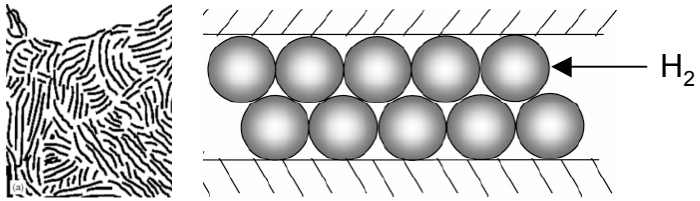




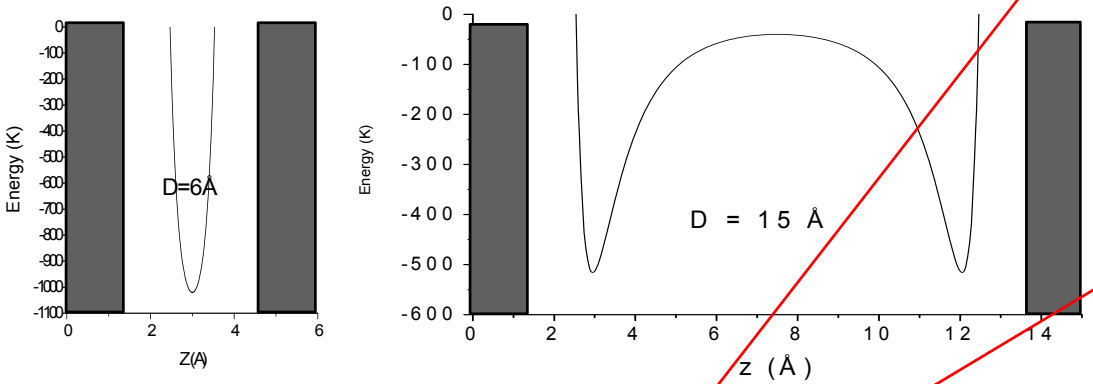
Materials synthesis and performance: boron-free carbons, cont.'d

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

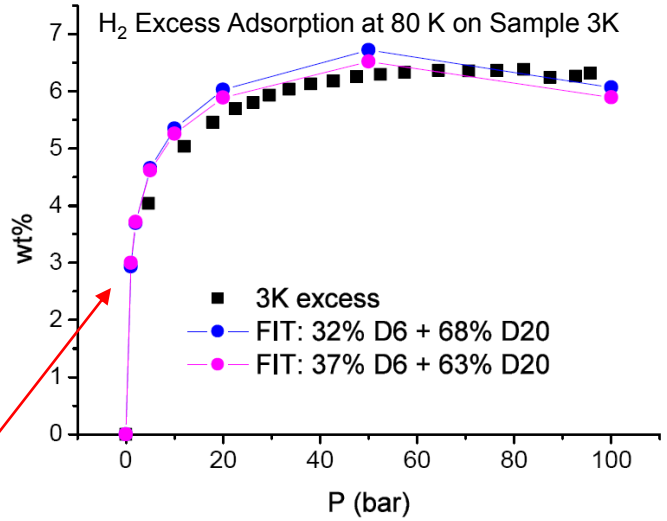
- Preparation of carbons suggests approximately slit-shaped pores reminiscent of exfoliated graphite
- Predominant pore width: 0.7-1.2 nm (see materials characterization)

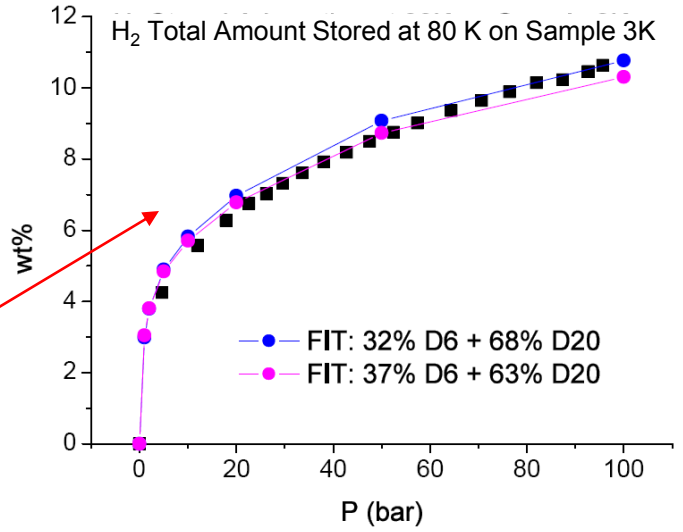


- Grand-canonical Monte Carlo (GCMC) simulations of H_2 adsorption in slit-shaped pores of width 0.6 nm (E_B = 9.0 kJ/mol) and 2.0 nm (E_B = 4.5 kJ/mol), with Σ = 2600 m^2/g (Kuchta & Firlej):



- 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





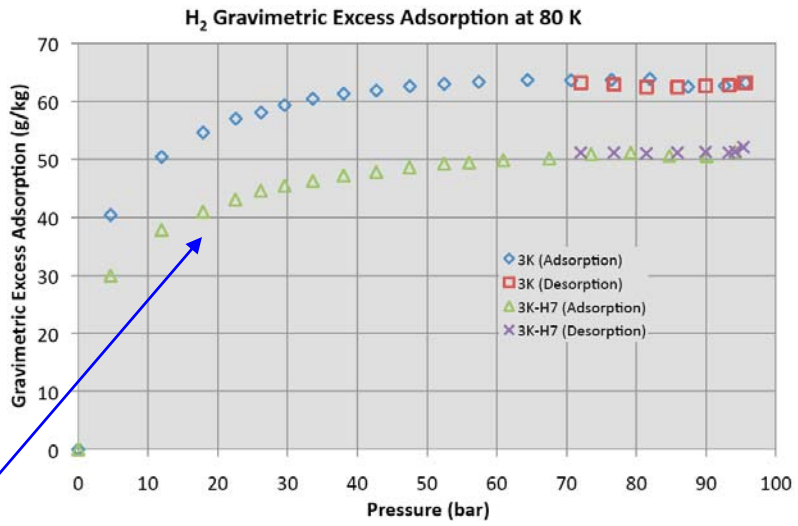
Materials synthesis and performance: boron-substituted carbons

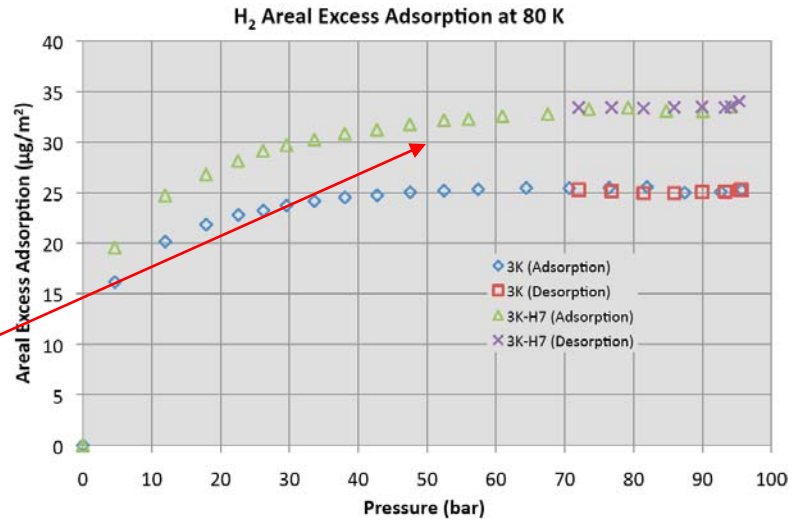
Boron substitution by deposition/decomposition of decaborane ($B_{10}H_{14}$)

- 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" + $B_{10}H_{14}$ $\xrightarrow{\text{Method I}}$ "3K-H7"	8.8 wt%	6.0 wt%	1500 m^2/g
"3K" + $B_{10}H_{14}$ $\xrightarrow{\text{Method II}}$ "3K-H6"	1.8 wt%	1.4 wt%	2400 m^2/g
"3K" + $B_{10}H_{14}$ $\xrightarrow{\text{Method III}}$ "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.

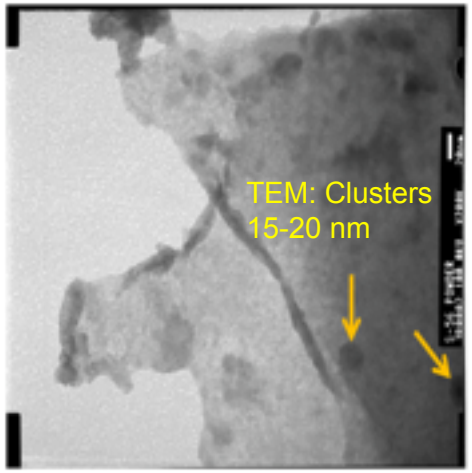




Materials synthesis and performance: magnetic carbons

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%

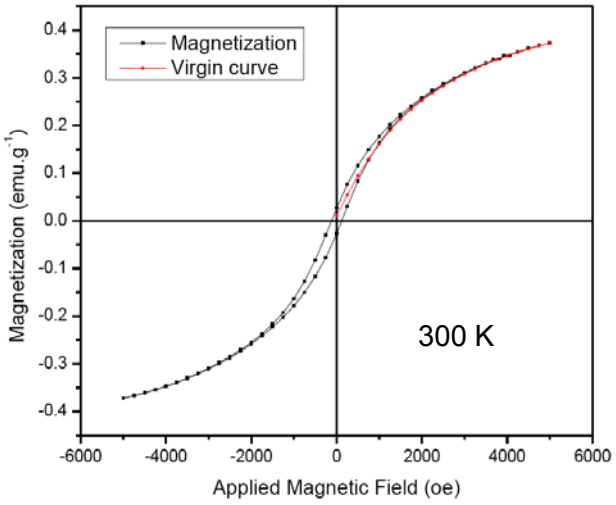
Corncob

Char before KOH treatment

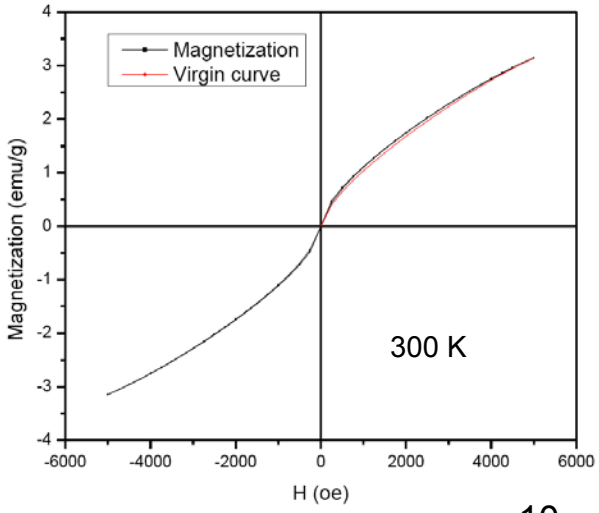
Carbon (3K) after KOH treatment in steel reactor

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

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



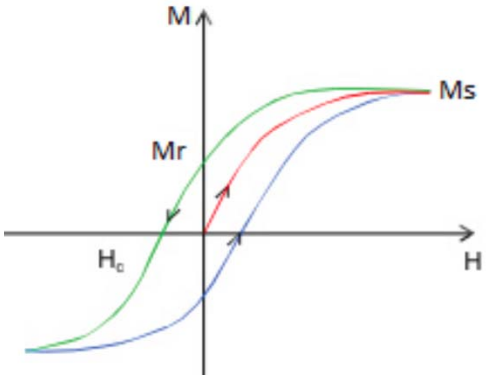
Sample Batch 5.32 is super-paramagnetic at 300 K (zero coercive field):



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

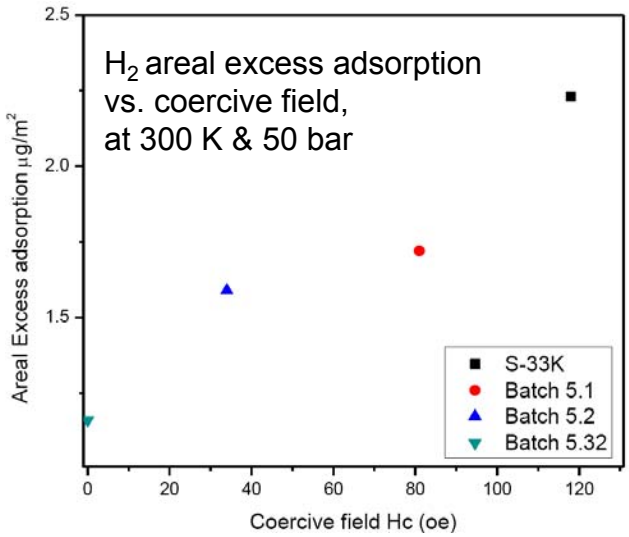
Magnetic properties of samples enhance H_2 adsorption (preliminary results)

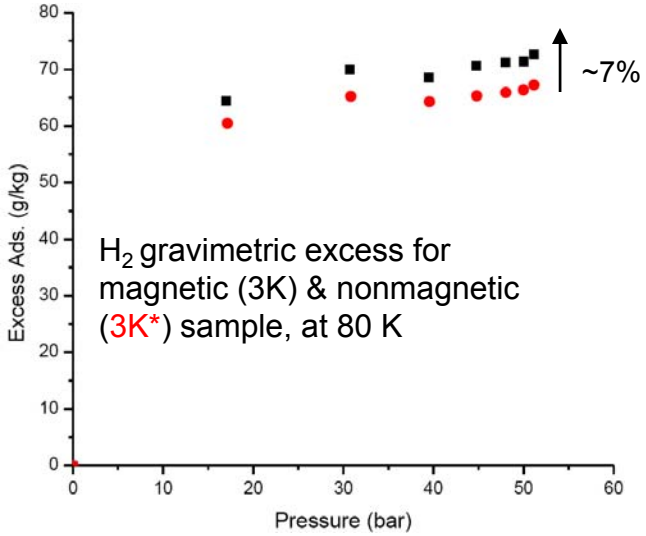
- Saturation magnetization, M_s, remnant magnetization, M_r, coercive field, H_c, and magnetic susceptibility, χ, at 300 K:



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	$5.25\cdot10^{-1}$	$5.65\cdot10^{-3}$

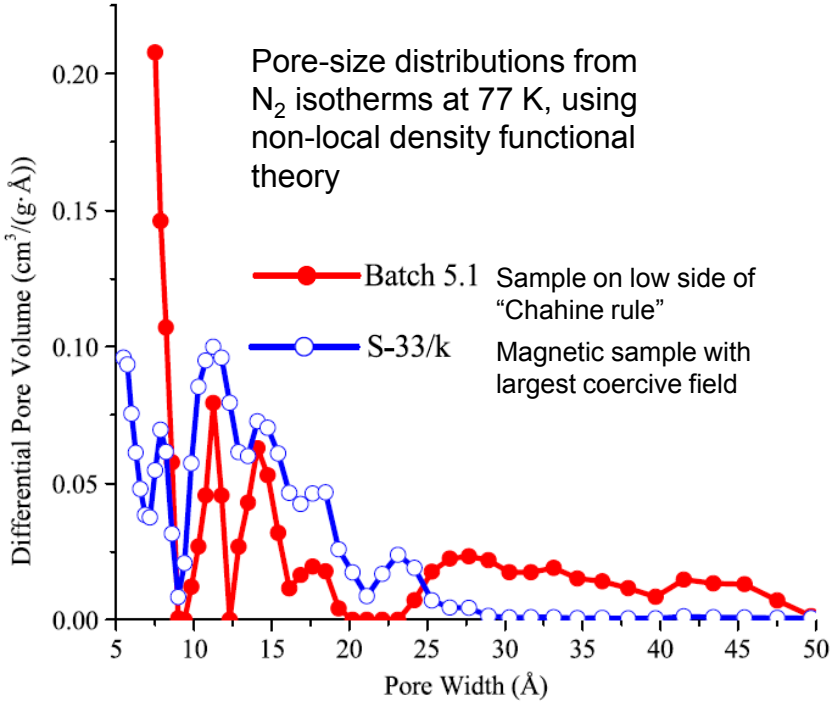
- Measured saturation magnetizations are consistent with Fe-induced magnetism: 0.5 wt% Fe in sample contributes 1.0 emu/g for Fe, and 0.7 emu/g for Fe_3O_4
- Larger coercive fields suggest larger size of magnetic clusters. S-33/k has largest coercive field at 300 K.

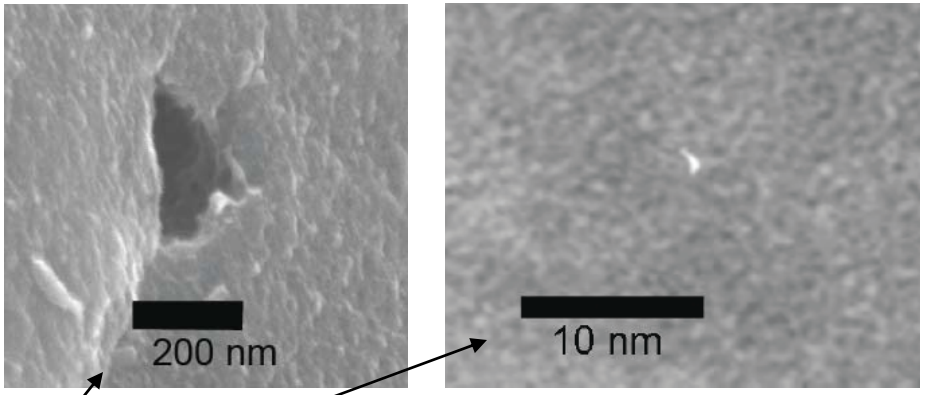




Structural characterization of samples

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:

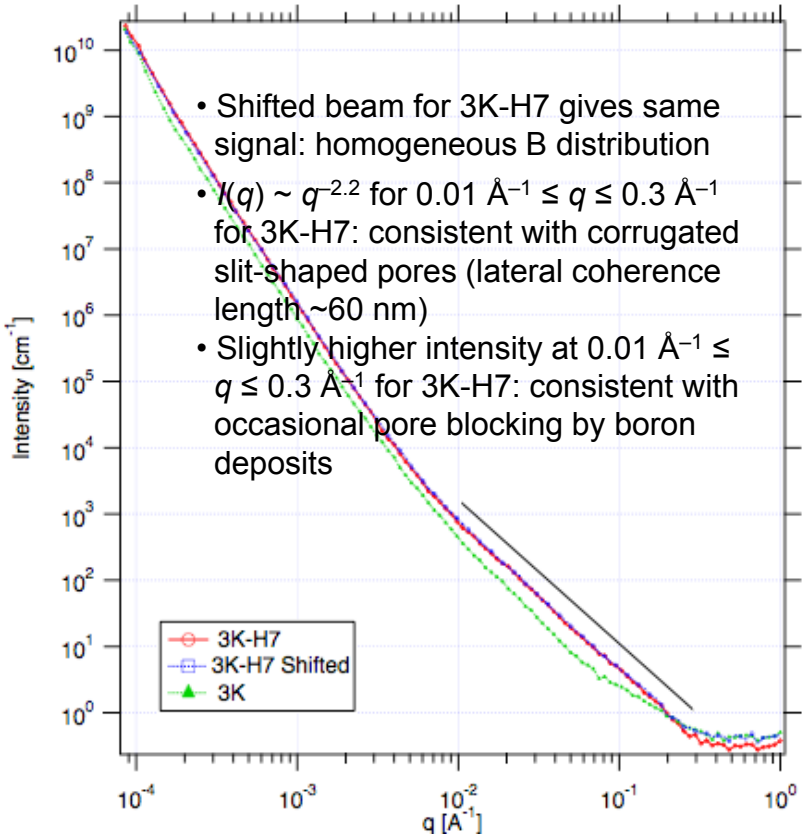
	Low energy (width ≥ 1.0 nm)	High energy (width <1.0 nm)
Prediction:	~5 kJ/mol	~8 kJ/mol
Exp./Batch 5.1:	4.8 kJ/mol	9.0 kJ/mol
Exp./S-33/k:	6.4 kJ/mol	8.6 kJ/mol

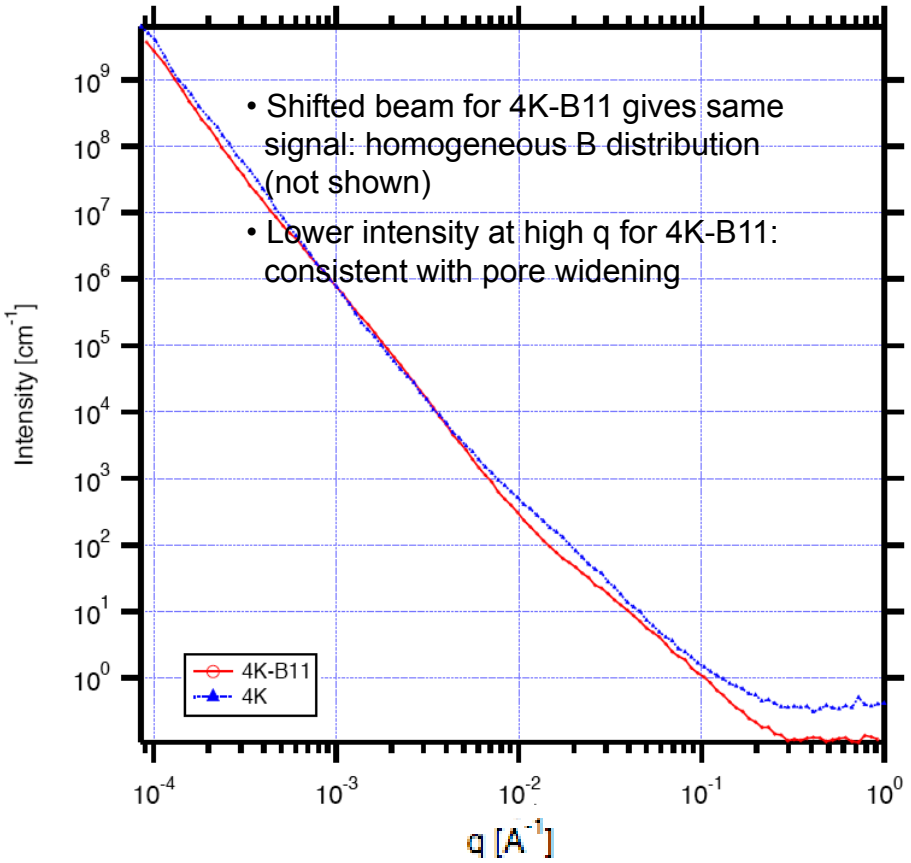
Structural characterization of samples, cont.'d

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

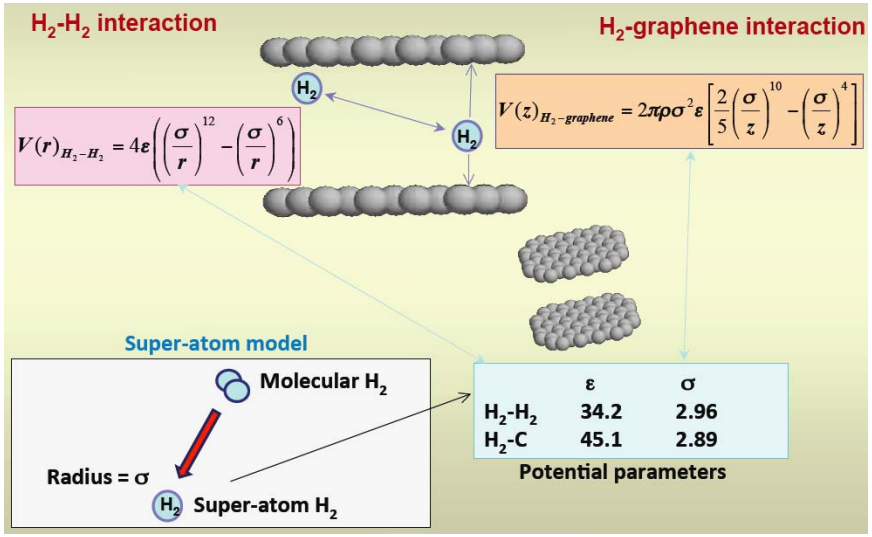
Sample 3K: B-free carbon, KOH activation; 2500 m^2/g
Sample 3K-H7: thermolysis of $B_{10}H_{14}$ on 3K; 6 wt% B (PGAA); 1500 m^2/g

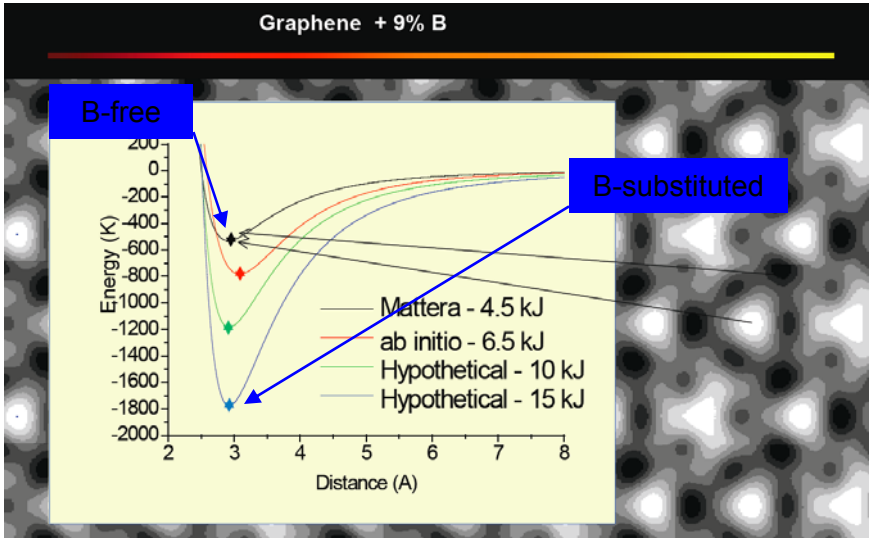
Sample 4K: B-free carbon, KOH activation; 2600 m^2/g
Sample 4K-B11: B-substituted carbon, KOH/KBH_4 activation; 7 wt% B (PGAA); surface area TBD

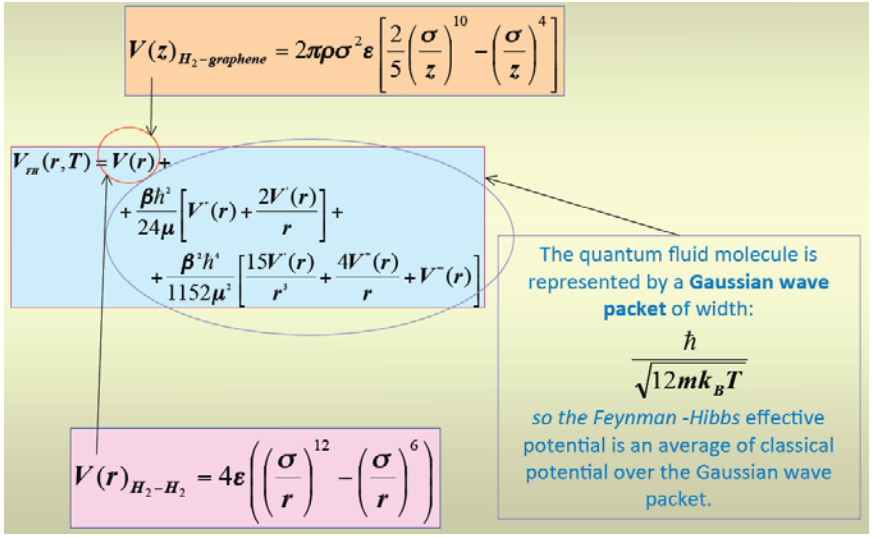


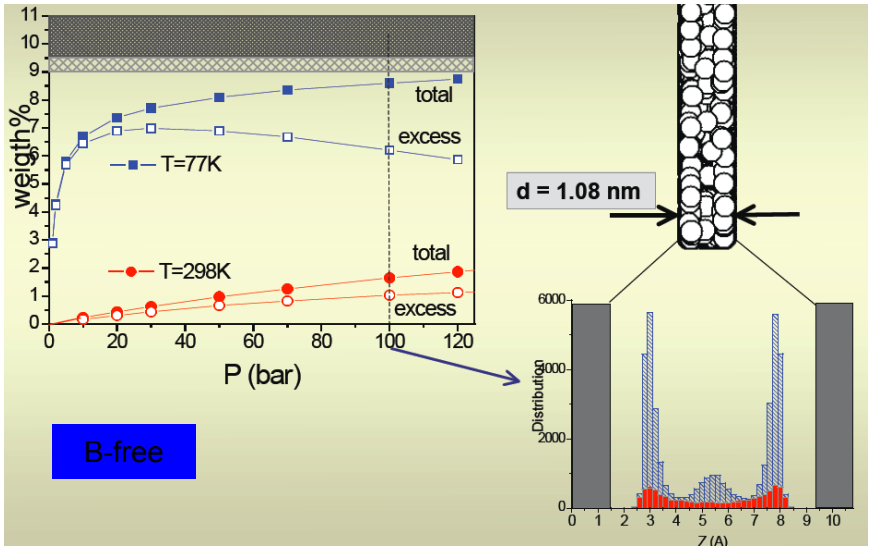


GCMC simulations in B-substituted materials

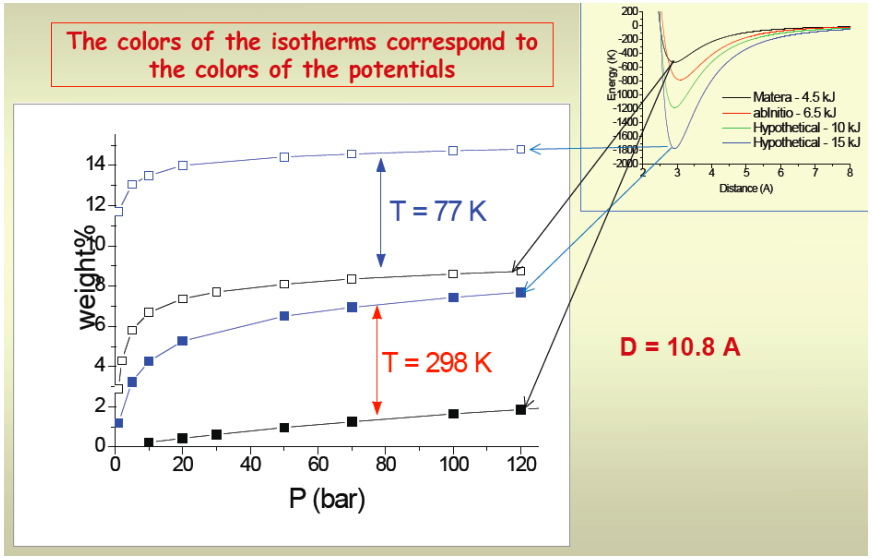


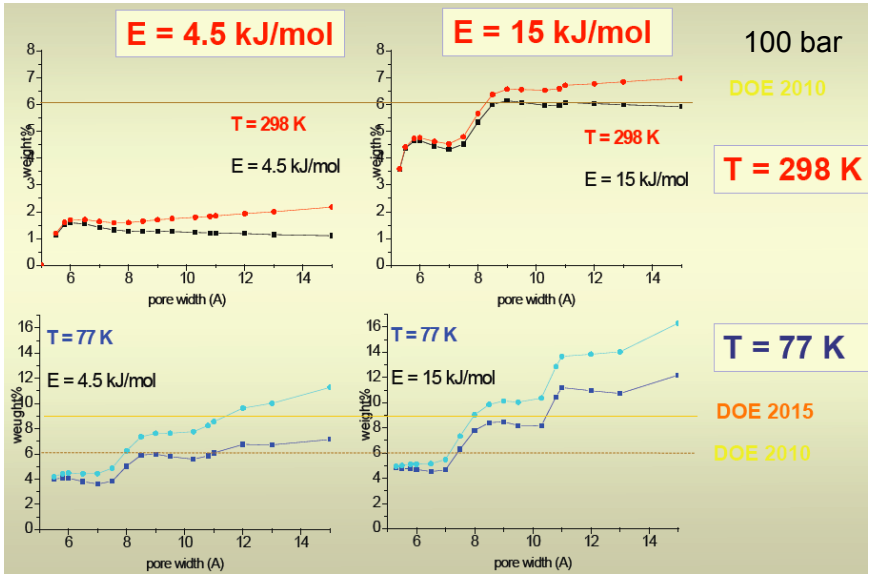


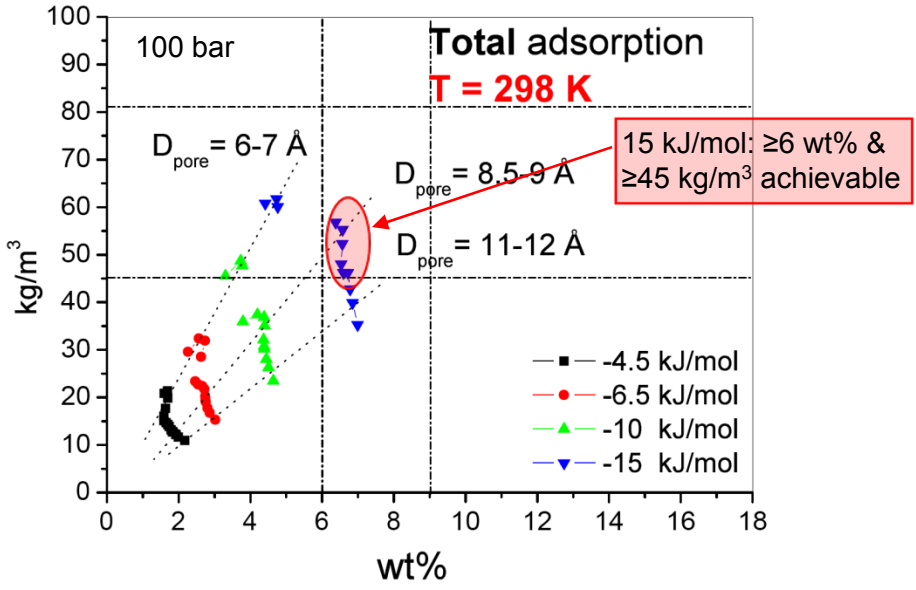


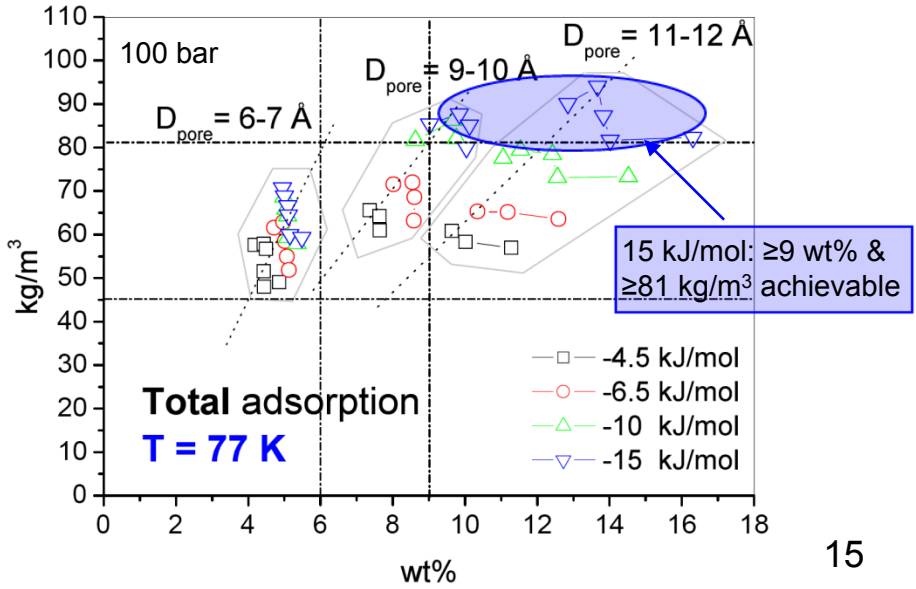


GCMC simulations in B-substituted materials, cont.'d









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.