Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Project ID #ST19

Overview

Timeline

- Project start date:
  - September 1, 2008
- Project end date:
  - November 30, 2014
- Percent complete: 80%

Budget

- **Total project funding**:
  - DOE share: $1,899K
  - Contractor share: $514K
- **Funding for FY 2012**
  - DOE share: $214K
  - Contractor share: $102K
- **Funding for FY 2013**
  - DOE share: $300K
  - Contractor share: $124K (est.)

Barriers

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

Partners

- T. Gennett, L. Simpson, P. Parilla – NREL
- R. Olsen – ORNL
- C. Brown, Y. Liu – NIST
- D. Waddill – Missouri U. Science & Technology
- L. Firlej – U. Montpellier II, France
- B. Kuchta – U. Marseille, France
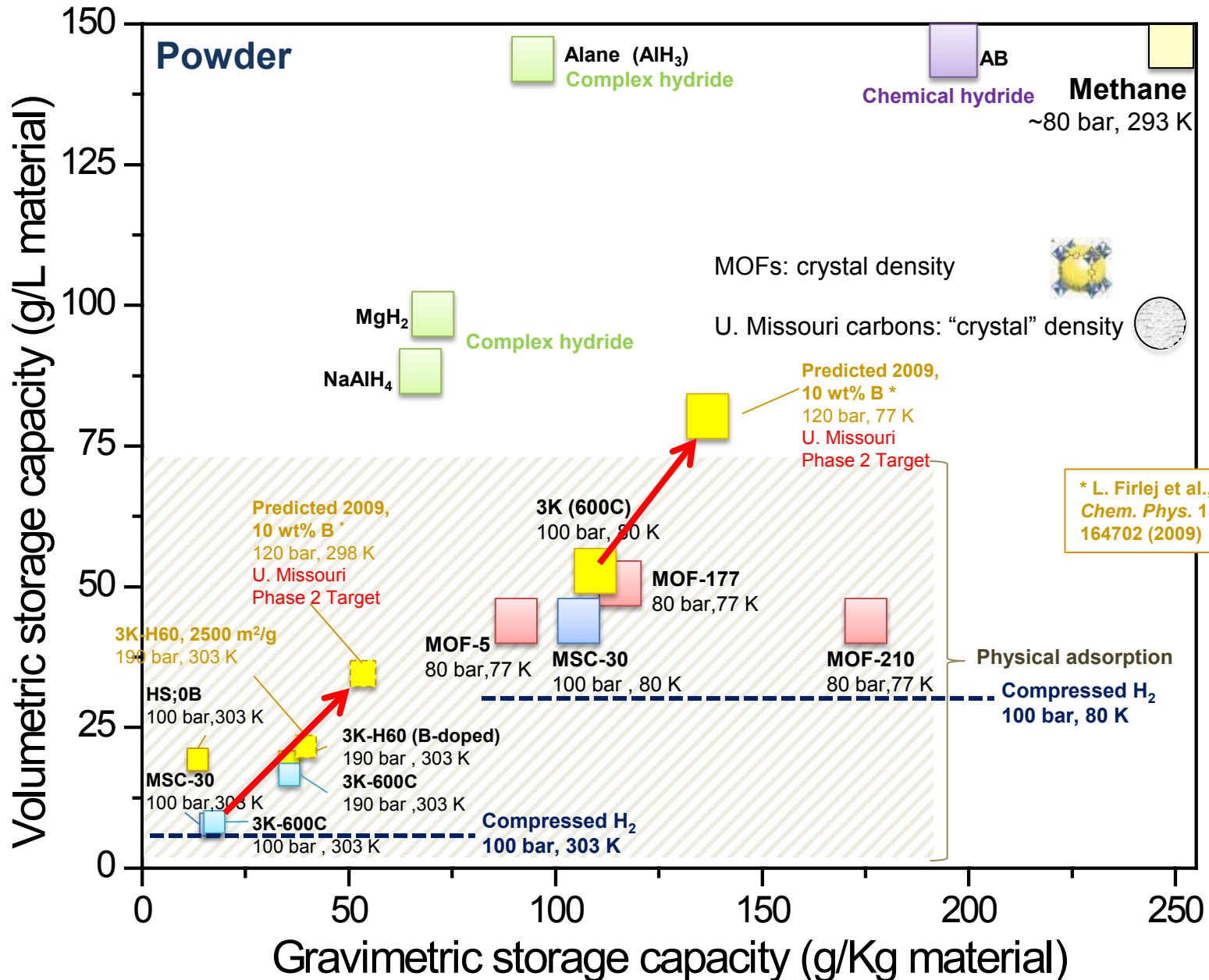
Objectives & Relevance

Fabricate boron-doped monolithic nanoporous carbon for high-capacity reversible hydrogen storage (March 2012-March 2013)

- Create high-surface-area monoliths with minimum pore space, for high volumetric storage capacity

- Dope materials with 0-20 wt% B:(B+C), for high binding energy for hydrogen

- Expect B-doped monoliths with surface areas ~ 2700 m^2/g, binding energies 10-15 kJ/mol, volumetric storage capacity >40 g/L (material), and gravimetric storage capacity >5.5 wt% (material) at 100 bar and room temperature

Characterize materials & demonstrate storage performance

- Establish high surface areas and low porosity of monoliths

- Establish uniform boron concentration in monoliths

- Establish that boron is completely substituted in carbon lattice (sp^2 B-C bonds; FTIR, XPS)

- Establish enhanced binding energy and H_2 adsorption on B-doped materials

- Determine H_2 sorption kinetics and temperature evolution during charging/discharging of monoliths

Relevance: Sorption Landscape

Powder

Alane (AlH$_3$)
Complex hydride

AB
Chemical hydride

Methane
~80 bar, 293 K

MOFs: crystal density

U. Missouri carbons: "crystal" density

MgH$_2$

Complex hydride

NaAlH$_4$

**Predicted 2009,
10 wt% B *
120 bar, 77 K
U. Missouri
Phase 2 Target**

**Predicted 2009,
10 wt% B *
120 bar, 298 K
U. Missouri
Phase 2 Target**

3K (600C)
100 bar, 80 K

MOF-177
80 bar, 77 K

3K-H60, 2500 m²/g
190 bar, 303 K

MOF-5
80 bar, 77 K

MSC-30
100 bar, 80 K

MOF-210
80 bar, 77 K

HS;0B
100 bar, 303 K

3K-H60 (B-doped)
190 bar, 303 K

MSC-30
100 bar, 303 K

3K-600C
190 bar, 303 K

3K-600C
100 bar, 303 K

Physical adsorption

**Compressed H$_2$
100 bar, 80 K**

**Compressed H$_2$
100 bar, 303 K**

* L. Firlej et al., *J. Chem. Phys.* 131, 164702 (2009)

x-axis: Gravimetric storage capacity (g/Kg material)

y-axis: Volumetric storage capacity (g/L material)

Approach

| Phase 2 Tasks	Milestones
4—Manufacture, characterize, and optimize B-doped monoliths	
4.1—Optimize B-doping of best U. Missouri carbon powder in region 0-20 wt% B:(B+C)	FY 2013 • Protocol for optimum B-doping path; lowest B:C above which further B does not improve H_2 adsorption • Establish B-doped carbon powders with $\Delta H > 12$ kJ/mol, and boron conc. >10 wt%, completely substituted within carbon lattice
4.2—B-dope current U. Missouri monoliths and characterize H_2 storage	FY 2013 • Establish uniform B-concentration in doped monoliths and that boron is completely substituted in carbon lattice • Establish that performance of doped monoliths is comparable to doped powders
4.3—B-dope alternate powder precursors and respective monoliths	FY 2014 Establish that Task 4.1/4.2-doped materials are superior to alternate doped materials
4.4—Measure H_2 storage and kinetics on B-doped monoliths in 0.5-liter H_2 Test Fixture at 295 K and on Sievert apparatus at 77 K	FY 2014 1. Establish B-doped monoliths with $\Sigma \sim 2700$ m^2/g, $\Delta H = 10\text{-}15$ kJ/mol, gravimetric storage capacity >5.5 wt% (material), volumetric storage capacity >40 g/L, at 100 bar & 295 K 2. Establish B-doped monoliths with $\Sigma \sim 2700$ m^2/g, $\Delta H = 10\text{-}15$ kJ/mol, gravimetric storage capacity >12 wt%

Technical Accomplishments

Best Performing Carbons

	Max. Grav. Excess (wt. % material)	Gravimetric Storage (wt. %, material)	Volumetric Storage (g/L material)	Surface Area (m²/g)	Isoteric Heat (kJ/mol)
3K-600C, **80 K**, 200 bar	6.3 (60 bar)	**12.0**	**63**	2,500	-
3K-600C, 303 K, 200 bar	1.2	3.3	16	2,500	Zero coverage: 7 High coverage: 6
4K Monolith (25% binder), 297 K, 100 bar	0.86	2.5	**9.5**	2,100	-
3K-120C, **1.5 kg tank**, 296 K, 100 bar	0.80	**3.0**	8.8	2,600	-
3K-H60 (I,A), **B:C = 8.9%** 303 K, 200 bar	1.5	**3.4**	**18**	2,100	**Zero coverage: 17 High coverage: 10**
Predicted 2009 (**B:C = 10%**, 2600 m²/g), 303 K, 120 bar	-	5.2	33	2,600	10-12

B-doped carbons show strong potential to meet DOE targets at room temperature

Technical Accomplishments

FY 2012 Ann. Prog. Rep.: B-doped 3K-H60(I,A), 8.9 wt% B
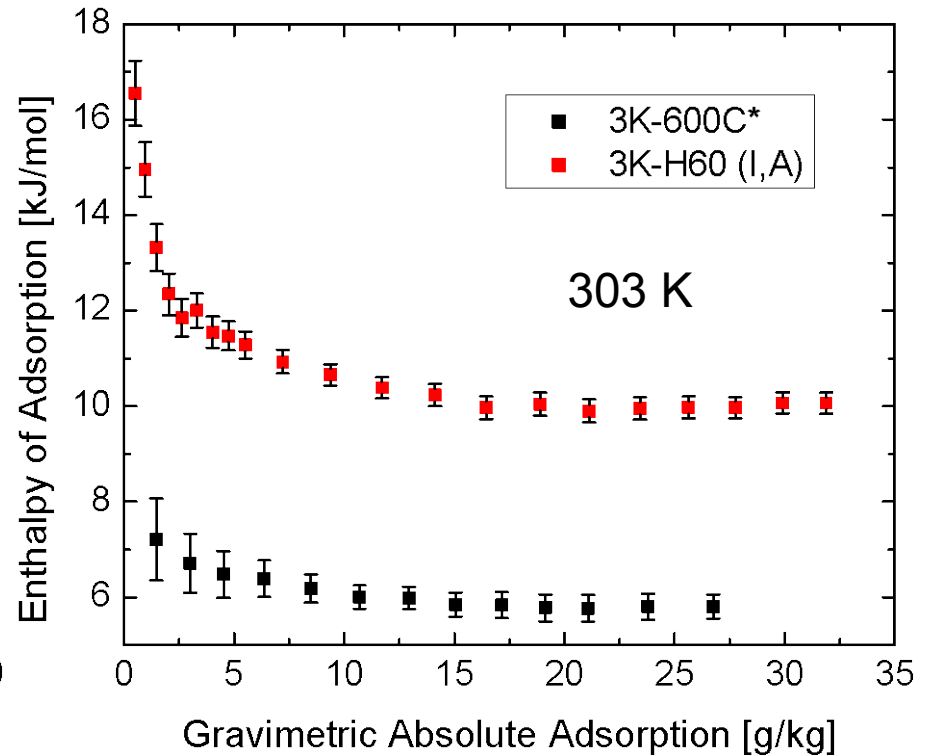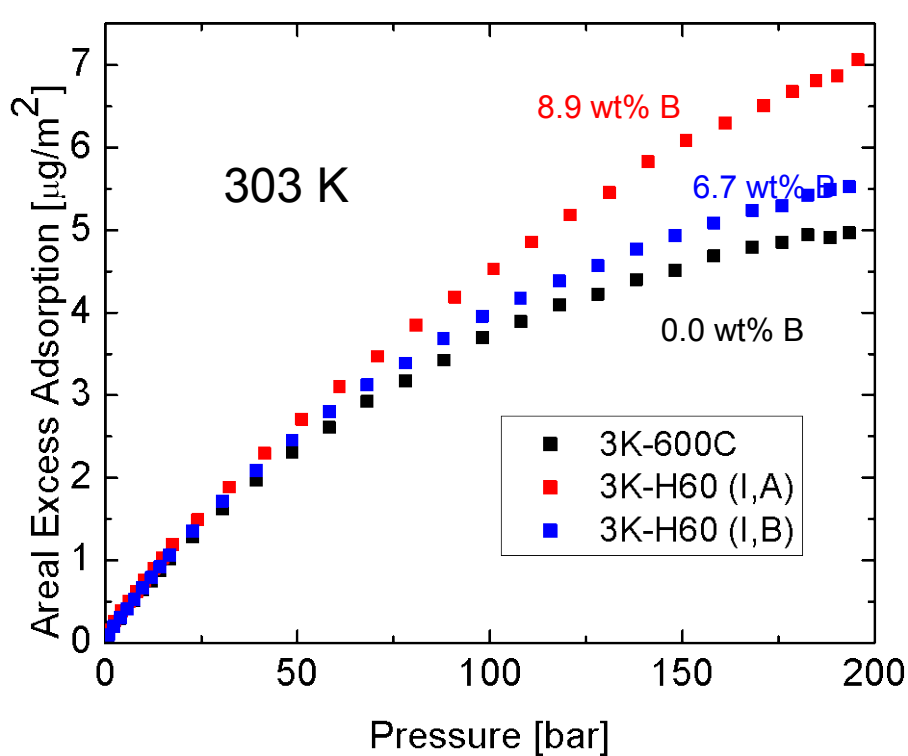
- H$_2$ excess adsorption per unit surface area (areal excess adsorption, AEA) depends only on how strongly surface binds H$_2$, not on surface area or pore volume. 40% increase in AEA at 200 bar: high binding energies on majority of surface sites

- Enthalpy of adsorption, ΔH, increased from 6 kJ/mol (0.0 wt% B) to 10 kJ/mol (8.9 wt% B)

- Film thickness t from ΔH analysis: t = 0.6 nm at 303 K (AMR 2010: t = 0.4 nm at 77 K)

- Task: Reproduce B-doped sample & high ΔH; validate at NREL

Technical Accomplishments

New U. Missouri undoped carbon: 3K-0046
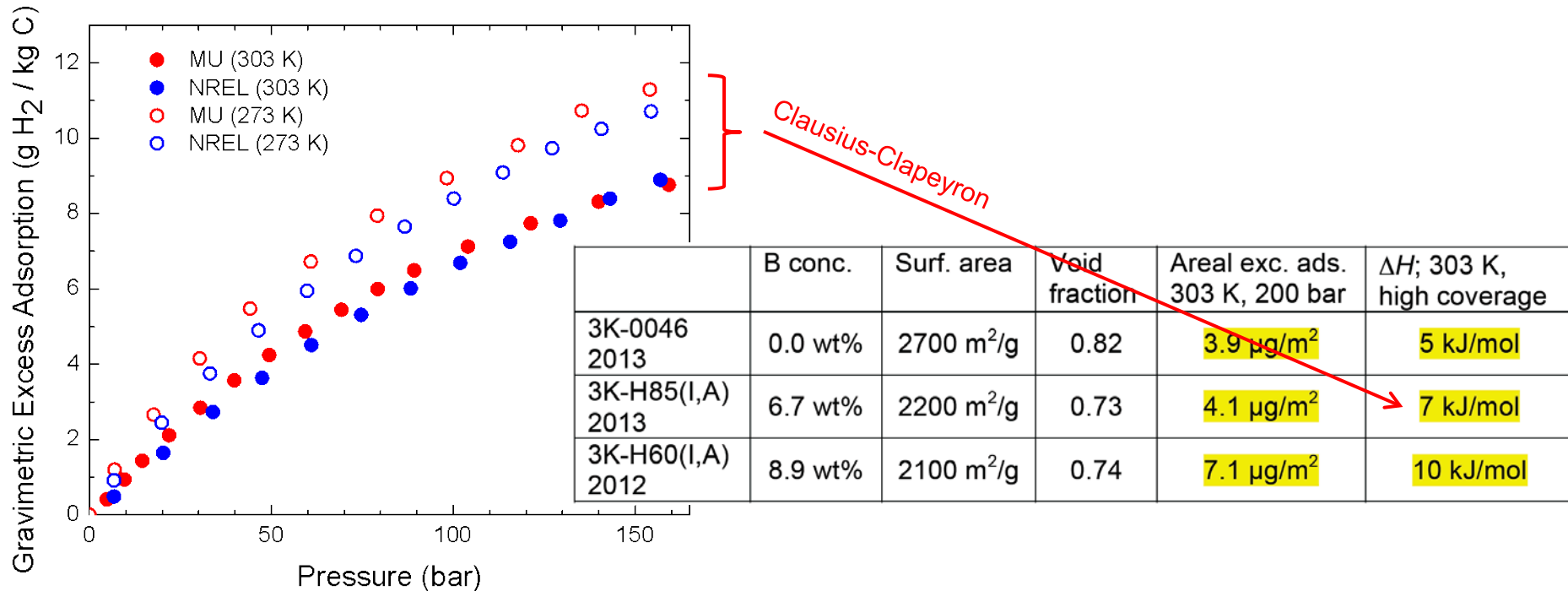

Room temperature
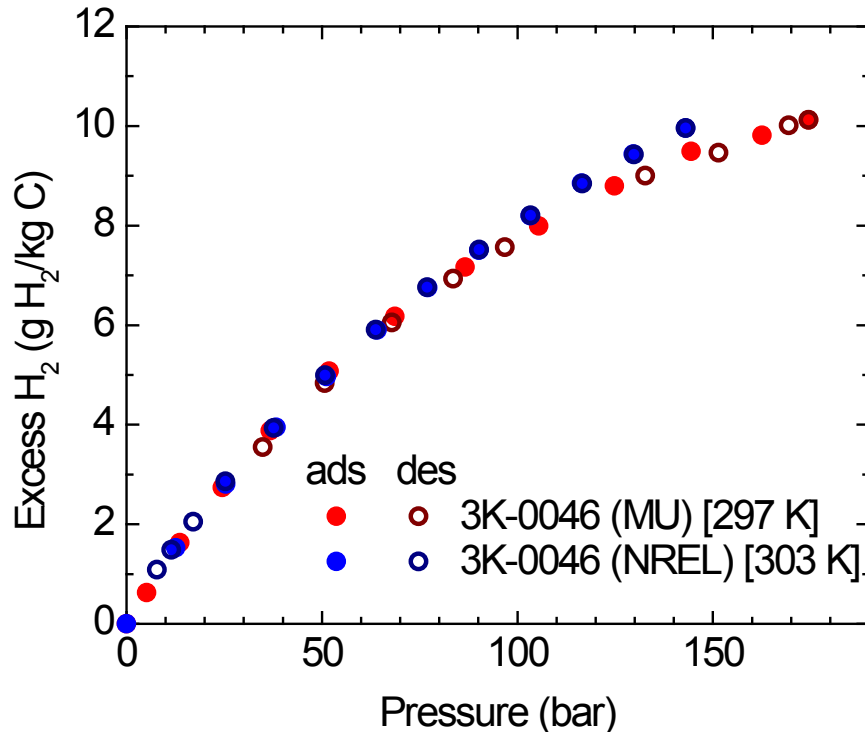
Liquid nitrogen (LN$_2$) temp.
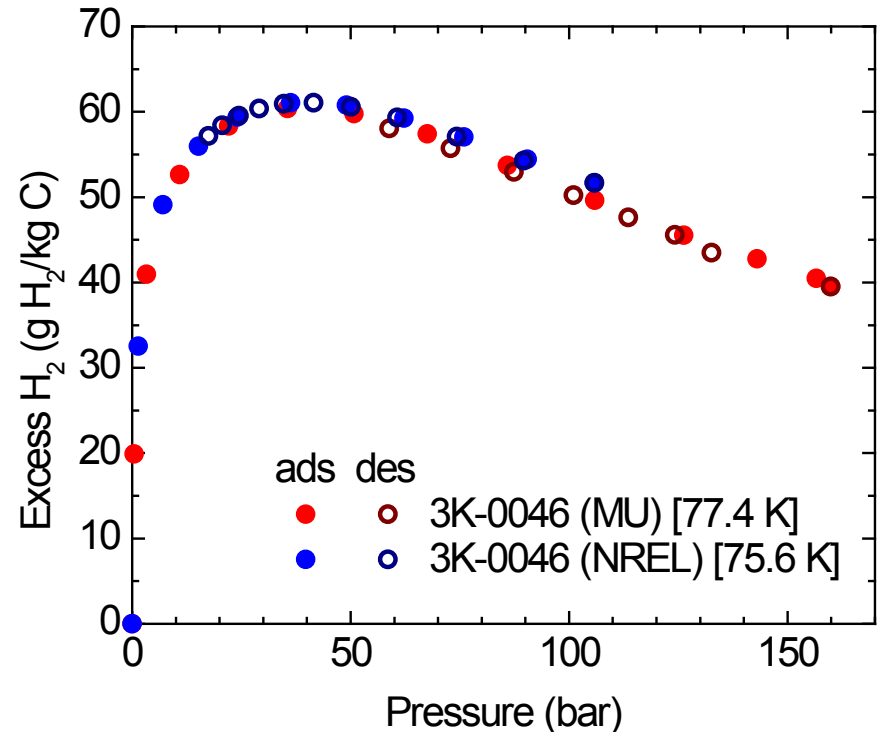
- Room temperature and LN$_2$ isotherms (adsorption and desorption) at NREL and U. Missouri agree; measured on same aliquot
- U. Missouri utilized LN$_2$ bath, replicating LN$_2$ bath at NREL
- Difference in LN$_2$ boiling temperature due to difference in elevation

Technical Accomplishments

New U. Missouri B-doped carbon: 3K-H85(I,A), 6.7 wt% B

	B conc.	Surf. area	Void fraction	Areal exc. ads. 303 K, 200 bar	ΔH; 303 K, high coverage
3K-0046 2013	0.0 wt%	2700 m²/g	0.82	3.9 µg/m²	5 kJ/mol
3K-H85(I,A) 2013	6.7 wt%	2200 m²/g	0.73	4.1 µg/m²	7 kJ/mol
3K-H60(I,A) 2012	8.9 wt%	2100 m²/g	0.74	7.1 µg/m²	10 kJ/mol

- 30 ºC and 0 ºC isotherms at NREL and U. Missouri agree
- Reproduced: B-doping/annealing (600 ºC) reduces surface area by <20%
- Reproduced: Both AEA and ΔH increase with increasing B concentration
- AEA, ΔH increase nonlinearly: largest increase from 6.7 to 8.9 wt% B
- 3K-H85(I,A): ΔH increased from 5 kJ/mol (0.0 wt% B) to 7 kJ/mol (6.7 wt% B)
- 3K-H60(I,A): ΔH increased from 6 kJ/mol (0.0 wt% B) to 10 kJ/mol (8.9 wt% B)
- Possible reason for nonlinearity: free-radical B atoms in 3K-H85(I,A) may have been converted to B⁻ anions

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Technical Accomplishments

B-doping monitored by x-ray photoelectron spectroscopy (XPS)
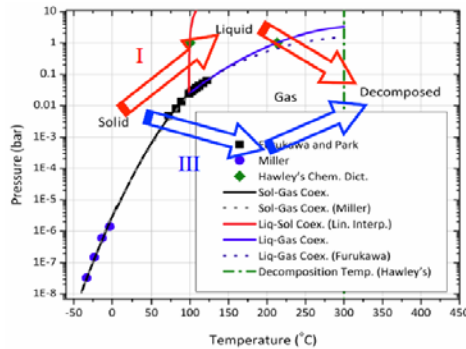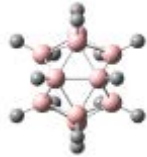
0. Decaborane/carbon mixture
1. Decaborane is deposited, but has not reacted
2. Decaborane reacts/decomposes
3. After annealing at 600 ^{0} C: 3K-H89(I,A), 8.6 wt% B

XPS spectrum
B1s electrons
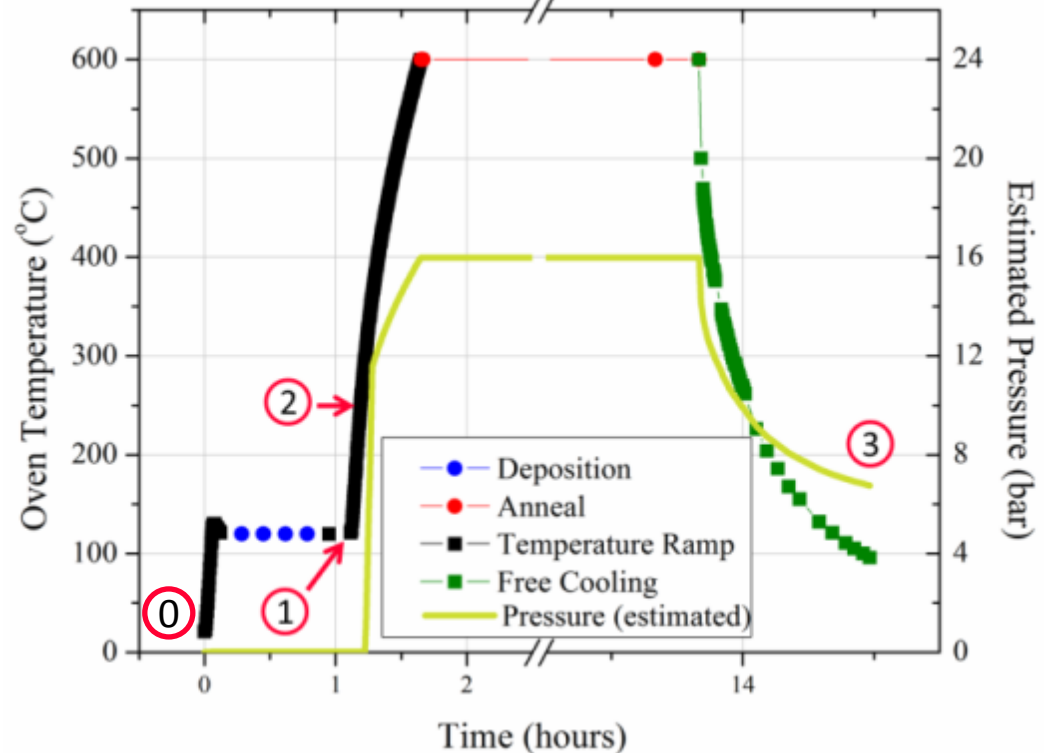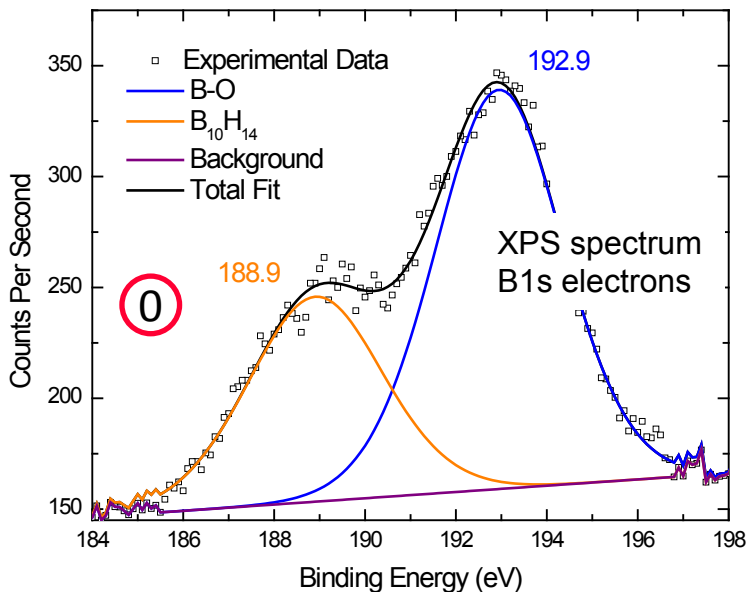
- Observed: expected $B_{10}H_{14}$ peak at 189 eV
- Observed: unexpected peak at 193 eV; attributed to B-O bonds from reaction of $B_{10}H_{14}$ with oxygen in air (transfer to sample chamber) or in carbon
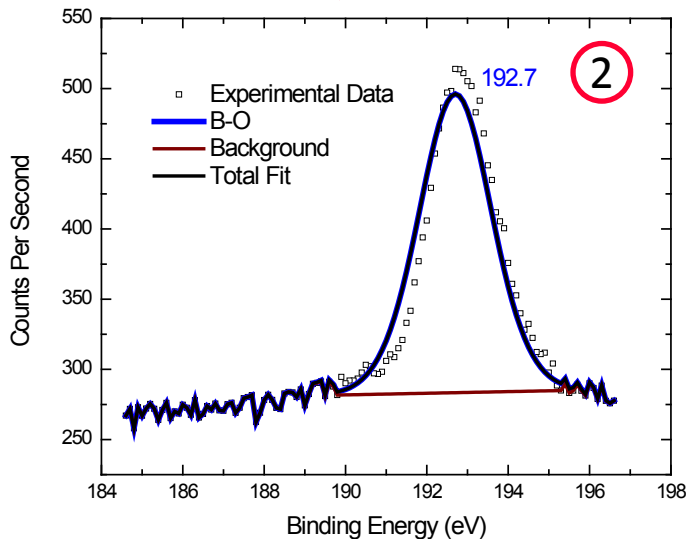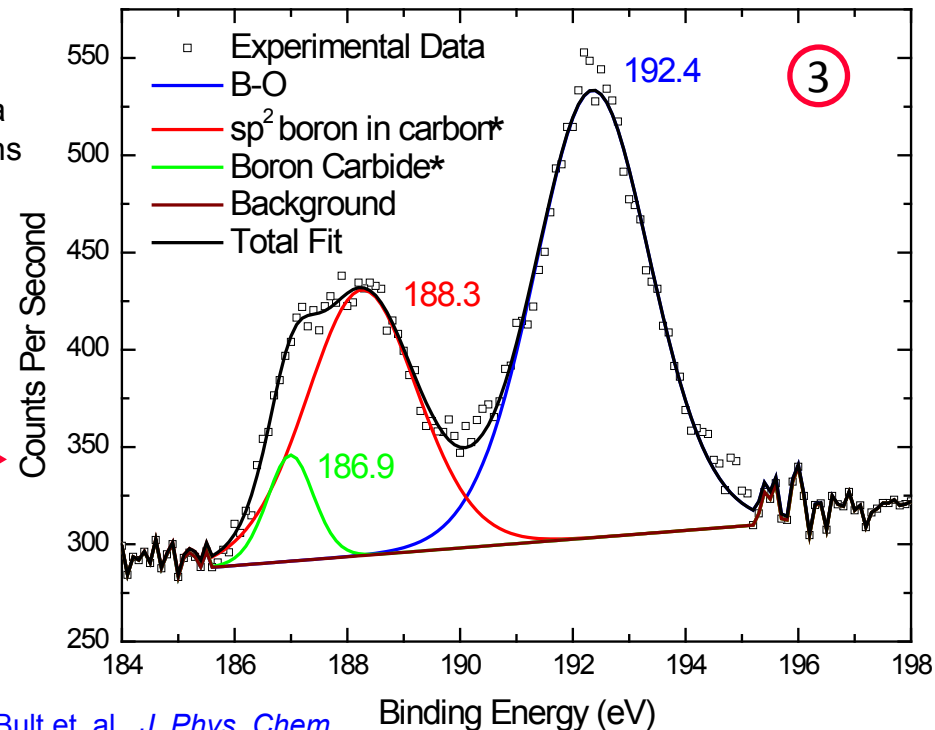
Technical Accomplishments

Deposition at 120 °C

At 250 °C

Anneal at 600 °C
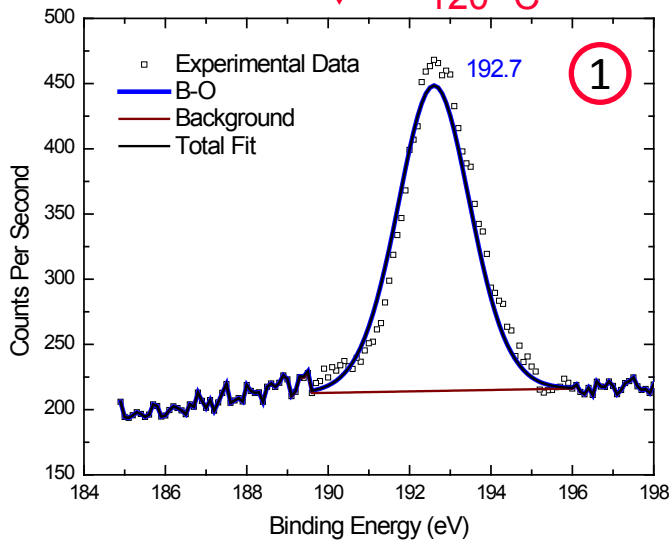
- 120 °C, no $B_{10}H_{14}$: $B_{10}H_{14}$ evaporated in XPS UHV chamber
- 250 °C, no B-C or B-B peak: $B_{10}H_{14}$ has not decomposed yet
- Final material, 3K-H89(I,A), 8.6 wt% B:
  - 188 eV peak: sp^2 B-C bonds [*]; enhanced binding of H_2
  - 187 eV peak: B_4C B-C bonds [*]; unenhanced binding of H_2
  - 6 out of 7 B-C bonds are sp^2 bonds
  - B-B bonds: may be present, but buried under B-C peaks
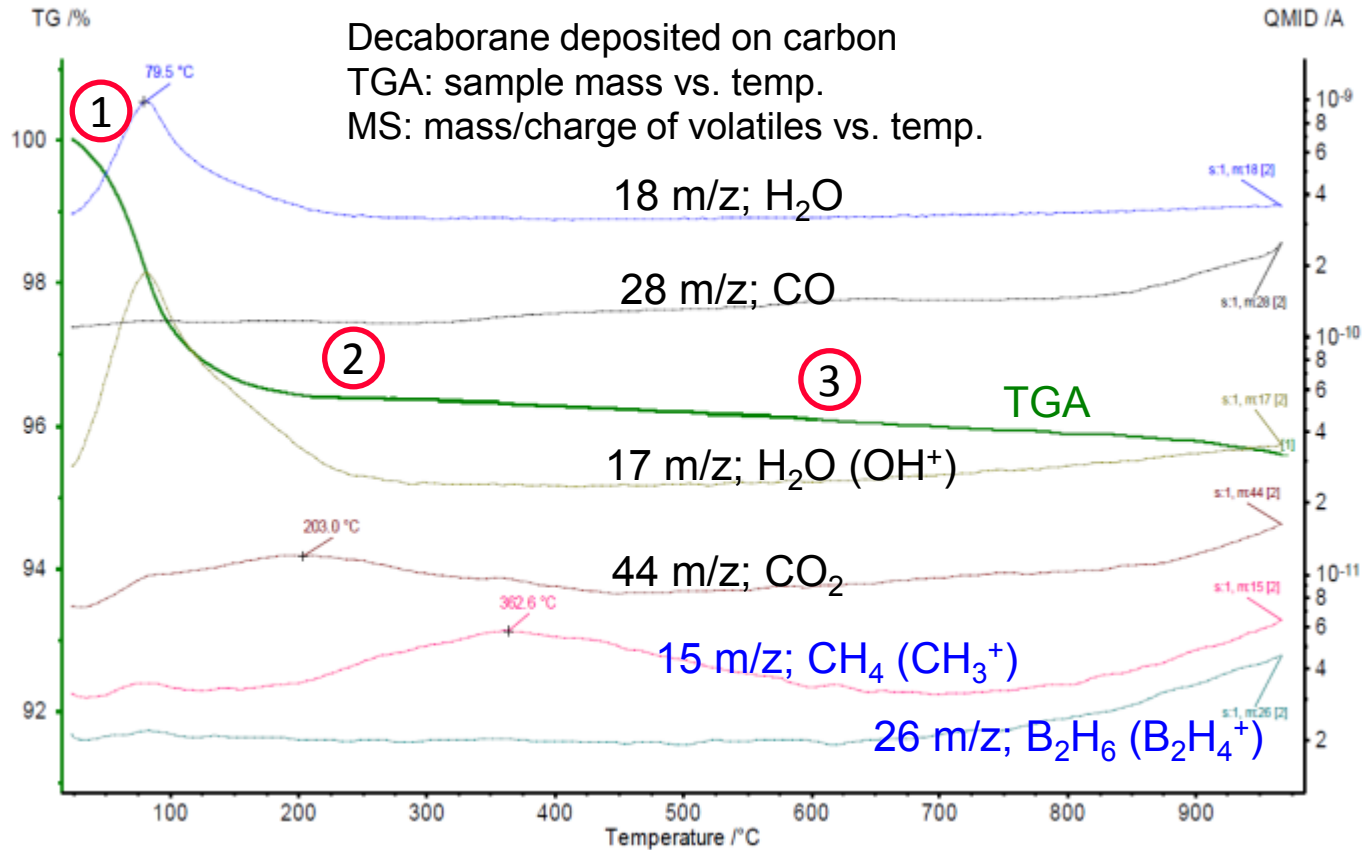 - 192 eV peak: B-O bonds survive at 600 °C (undesirable)

XPS spectra B1s electrons

* Bult et. al., *J. Phys. Chem C* **116**, 26138 (2012)

Technical Accomplishments

Thermogravimetric analysis/mass spectroscopy: 3K-H89(I,A), 8.6 wt% B

Decaborane deposited on carbon
TGA: sample mass vs. temp.
MS: mass/charge of volatiles vs. temp.

18 m/z; H_2O

28 m/z; CO

TGA

17 m/z; H_2O (OH^+)

44 m/z; CO_2

15 m/z; CH_4 (CH_3^+)

26 m/z; B_2H_6 ($B_2H_4^+$)

TG /% — Temperature /°C — QMID /A

- H_2O, CO, CO_2: from sample exposure to air & removal of surface-bound oxygen
- 350 °C: CH_4 from decomposition of $B_{10}H_{14}$ on C
- 600-1000 °C: boron loss in form of B_2H_6
- Boron loss, from 8.9 to 6.7 wt%, at 600-1000 °C, observed previously by PGAA
- Rise of CO, CO_2 at >600 °C: removal of surface-O requires >600 °C, also on B-free carbons

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Technical Accomplishments

B-C bonds from microscopic Fourier transform infrared spectroscopy (FTIR)

New B-doped samples: 3K-H82(I,A), 3K-H82(I,B)
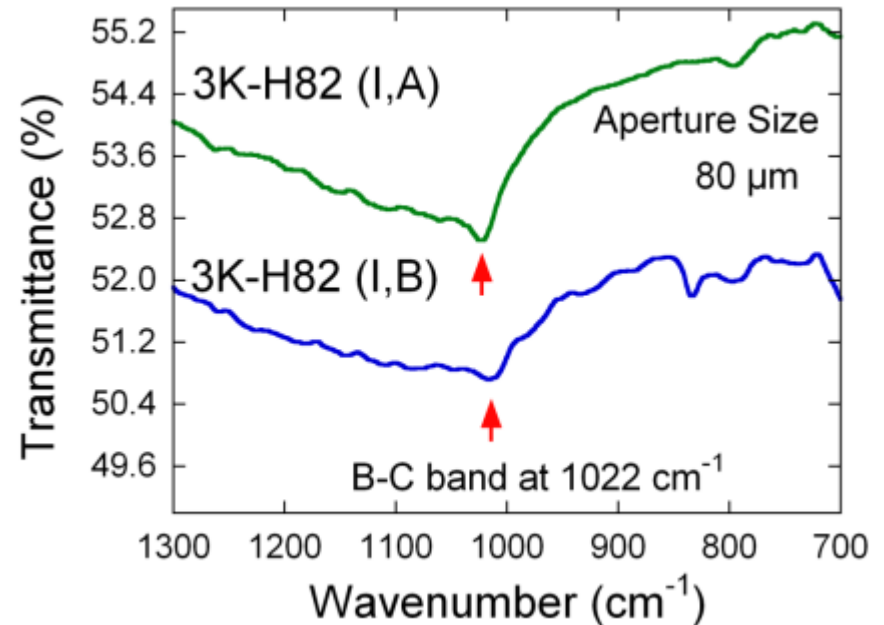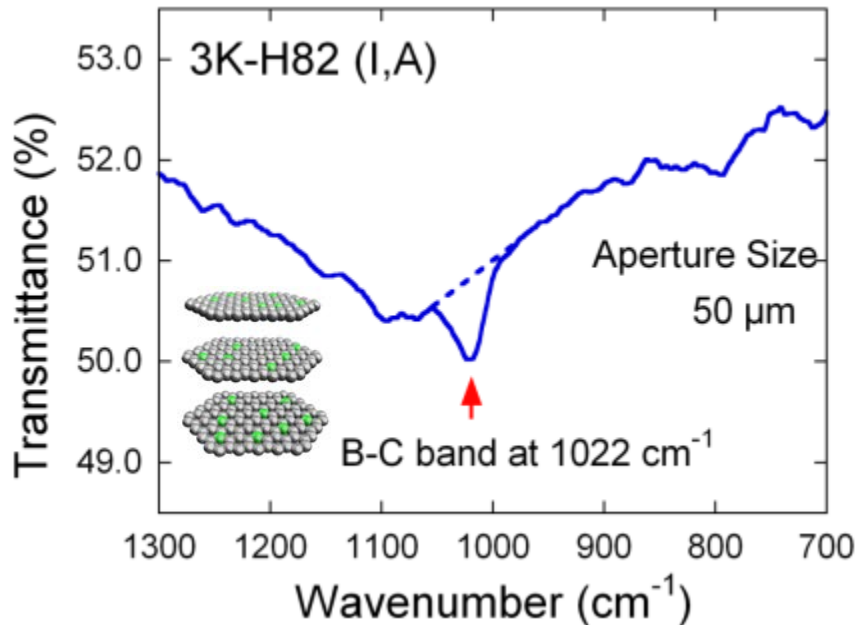
	wt% B
3K-H82(I,A): annealed at 600 ºC	6.7
3K-H82(I,B): annealed at 1000 ºC	4.4

- Improved resolution of B-C band by careful sample post-treatment & aperture selection
- B-C band position does not change with sample preparation (2012, 2013) and annealing temp.: same B-C bonds in all samples
- Smaller signal in 4.4 wt% B than in 6.7 wt%: FTIR can quantify conc. of B-C bonds in sample

Technical Accomplishments

Fabrication of B-doped monoliths

- Objective 1: Create high-surface-area, high-density monoliths (sub-nm pores only), for high volumetric storage capacity. In addition: sub-nm pores host high H_2 binding energies
- Objective 2: Dope monoliths with 0-20 wt% B, for high H_2 binding energy
- Objective 3: Determine H_2 sorption kinetics and temperature evolution during charging/discharging of monoliths

- Achieved: First fabricate carbon monoliths from carbon powder, then B-dope by vapor deposition and pyrolysis of $B_{10}H_{14}$. Alternative—first B-dope powder, then fabricate monoliths—not pursued
- Achieved: $B_{10}H_{14}$ vapor penetrates monolith, but creates lower B-concentration inside (next slide)
- Expect (next slide): (i) Low B-concentration inside monolith can be improved (ii) Maximum monolith dimensions for uniform B-concentration in monolith
- Achieved: High binding energy on new undoped monoliths (next slides)

Technical Accomplishments

Spatial distribution of boron in doped monoliths
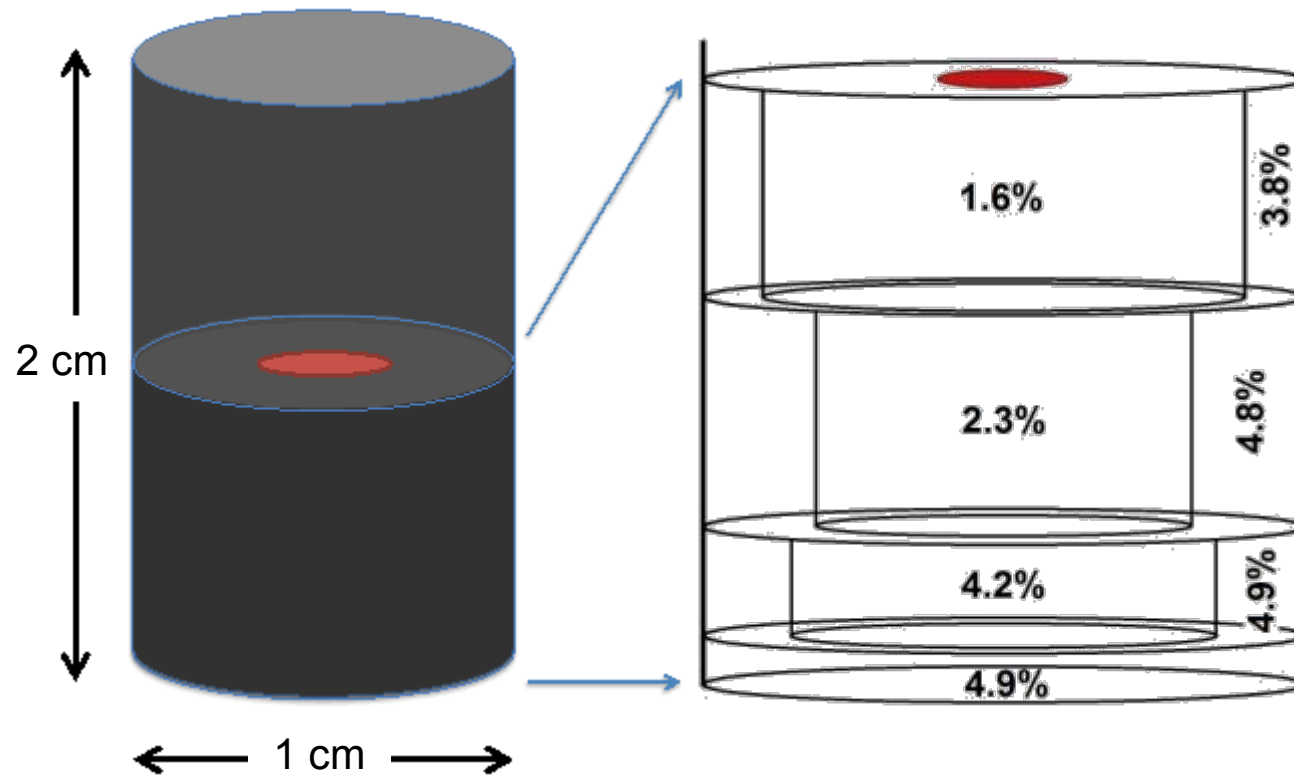
- 1 cm x 2 cm monolith, from 3.5"-inch monolith BR2.5K-0162, was B-doped with $B_{10}H_{14}$ (solid-liquid-gas route, I): 4.5 wt% B (total)
- Monolith was oriented vertically, with solid/liquid $B_{10}H_{14}$ underneath. Significant B-conc. gradients
- 4.2 wt% B at $(r, z) = (0\ cm, 0.25\ cm)$: successful doping from liquid phase
- 3.8 wt% B at $(r, z) = (0.45\ cm, 0.85\ cm)$: successful doping from gas phase
- Drop from 3.8 to 1.6 wt% B at $z = 0.85\ cm$: 5.8 wt%/cm. Reason: $B_{10}H_{14}$ on C: 70-80 kJ/mol (2012 AMR)
- Drop from 4.9 to 2.3 wt% B at $r = 0\ cm$: 4.4 wt%/cm
- Ongoing: (i) Dope suspended monoliths; (ii) Minimize diffusion-limited adsorption of $B_{10}H_{14}$ by using carrier gas (Ar)

Technical Accomplishments

New undoped 3.5" monoliths: improved H_2 performance
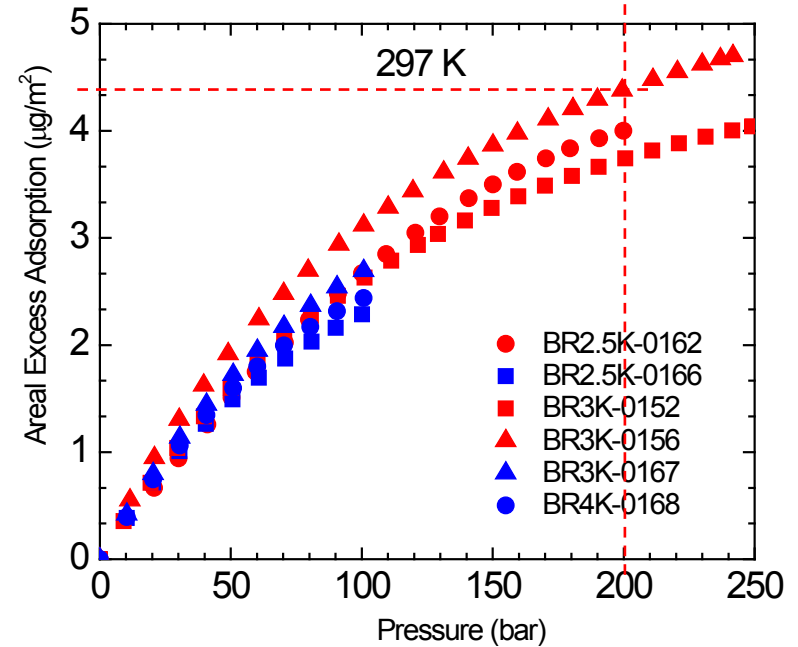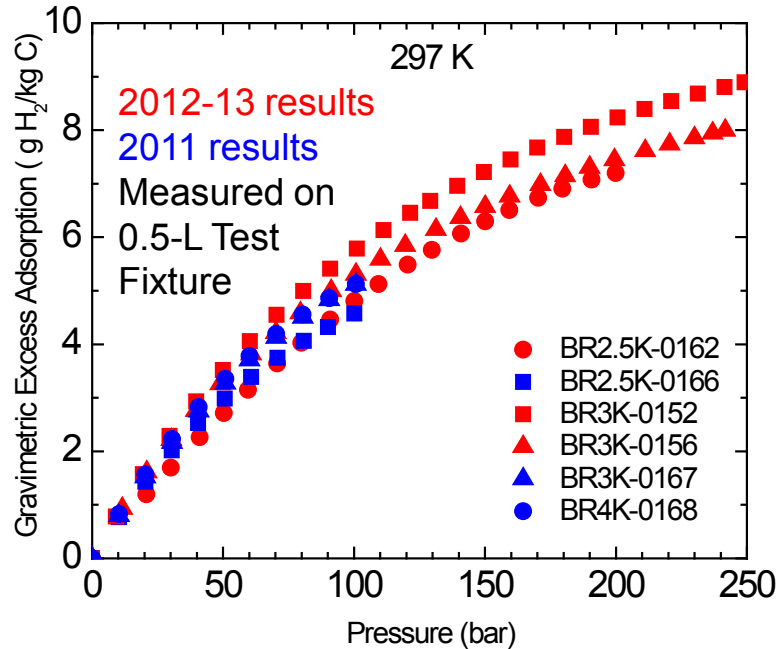
|	Binder: carbon (wt)	Compaction temp.	Pyrolysis temp.	Surface area	Porosity (N_2)
BR2.5K-0162	1.25	230 °C	750 °C	1800 m²/g	0.66
BR3K-0152	1.00	280 °C	750 °C	2200 m²/g	0.73
BR3K-0156	1.00	170 °C	850 °C	1700 m²/g	0.67

- Compaction at 230 ºC favors lower porosity, thus high volumetric storage capacity
- BR3K-0152: high gravimetric excess adsorption due to high surface area; but low areal excess adsorption (AEA) due to abundance of supra-nm pores
- BR3K-0156: high AEA (high binding energy) due to dominance of sub-nm pores
  AEA at 200 bar and room temp.: 4.3 µg/m²—higher than B-doped powder 3K-H85(I,A)
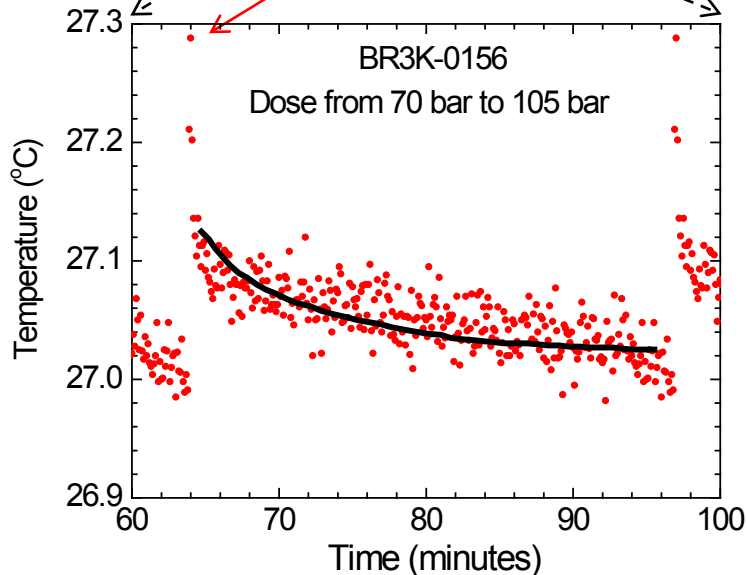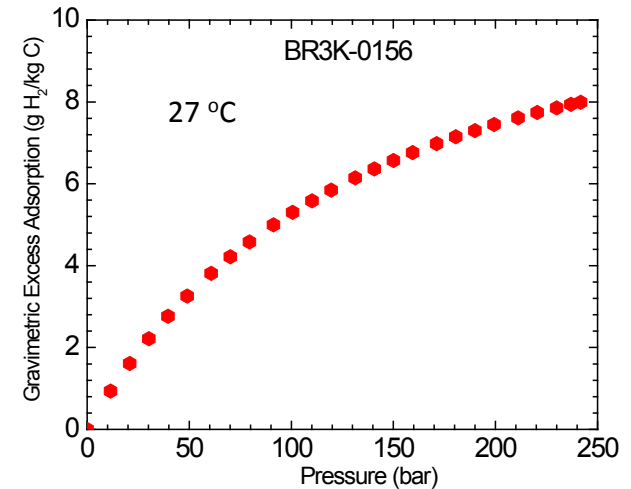
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Technical Accomplishments

Kinetics on undoped 3.5" monolith: charging/discharging rates, thermal management
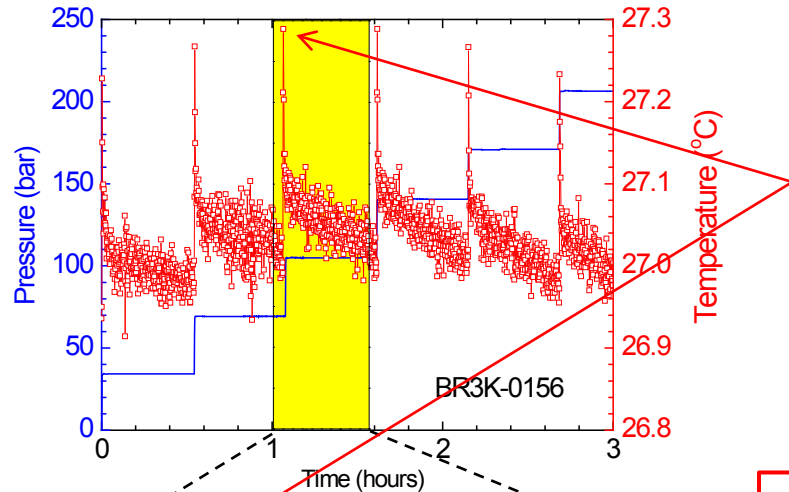
Heating due to adiabatic compression and heat of adsorption

BR3K-0156

Dose from 70 bar to 105 bar

- BR3K-0156: monolith (43 g) with highest binding energy
- Measurements in 0.5-L Test Fixture
- Charging in 35-bar/33-min steps: maximum temperature excursion: +0.3 ºC
- Excursion largest at 0-150 bar (heat of adsorption large when H_2 uptake large: low pressure)
- Temperature drops, from maximum (27.3 ºC), first exponentially with time constant of 2 min, then linearly at 0.2 ºC/h
- Drop because monolith in contact with large steel sample chamber (heat sink)

Collaborations

- **NREL** (Federal): L. Simpson, P. Parilla, T. Gennett—Validation of H_2 uptake

- **Advanced Photon Source/ANL** (Federal): J. Ilavsky—Ultra-small-angle x-ray scattering (GUP-10069, GUP-20661)

- **NIST** (Federal): Y. Liu, C. Brown—small-angle neutron scattering with in-situ, adsorbed H_2

- **U. Montpellier II** & **U. Marseille**, France (Academic): L. Firlej & B. Kuchta—GCMC simulations

- **Wroclaw U. Technology**, Poland (Academic): S. Roszak—adsorption potentials for H_2 sorption on B-doped materials from ab initio quantum-chemical computations

- **ORNL** (Federal): M. Stone, R. Olsen—incoherent inelastic neutron scattering with in-situ, adsorbed H_2

- **U. Marseille**, France (Academic): P. Llewellyn—micro-calorimetric determination of isosteric heat of adsorption

- **U. Missouri** (Academic): M. Greenlief—XPS analysis; J. Burress—sorption measurements; H. Taub, D. Robertson—neutron scattering & PGAA

- **Missouri U. of Science & Technology** (Academic): D. Waddill—XPS analysis

Future Work: Plans for 2013/14

- **Optimize B-doping of granular materials & demonstrate performance**

  - Improve oxygen-free preparation of undoped/doped carbon (deoxygenation and annealing at 1200 ºC)

  - Suppress conversion of B$^\bullet$ free radicals into B$^-$ anions; test B-doped materials for free radicals by electron paramagnetic resonance spectroscopy (EPR); determine XPS and FTIR spectra of anionic sp^2 B$^-$-C bonds on model compound; estimate H$_2$ binding energy on B$^-$-substituted carbon from quantum-chemical calculations

  - Monitor B-doping with XPS under oxygen-free conditions, NMR, and elemental mapping of B with energy-filtered transmission electron microscopy (EFTEM)

  - Map out enthalpy of adsorption, ΔH, and areal excess adsorption for H$_2$, at 77 K and 273 K, on B-doped powders with 0-20 wt% B. Improve determination of ΔH at high coverage from Clausius-Clapeyron

- **Optimize B-doping of monoliths & demonstrate performance**

  - Optimize undoped monoliths for high surface area and small pore volume

  - Improve B-doping of monoliths; minimize B-concentration gradients

  - Monitor B-doping by XPS, FTIR, EFTEM, NMR

  - Monitor performance of doped monoliths by ΔH and areal excess adsorption

Project Summary, 2012-13

- B-doped carbons at *room temperature*, *high coverage* (majority of surface sites)
  Unexpected nonlinear dependence of binding energy on B concentration:
  3K-H60(I,A), 8.9% wt% B: ΔH increased from 6 to 10 kJ/mol; AEA increased by 40%
  3K-H85(I,A), 6.7% wt% B: ΔH increased from 5 to 7 kJ/mol; AEA increased by 5%
  3K-H85(I,A): validated at NREL (77 K and RT)

- Highest surface area of B-doped materials to date: 2200 m^2/g
  Top AEA's to date (RT, 200 bar): 3.9, 4.1, 7.1 µg/m^2

- XPS established two types of B-C bonds: (a) sp^2 bonds (90%, enhance H_2 binding);
  (b) B_4C bonds (10%, do not enhance H_2 binding)

- XPS, TGA-MS, and PGAA established:
  – Presence of B-O bonds (inert up to 600 ºC)
  – Loss of B in form of B_2H_6 at 600-1000 ºC (20-30% loss)
  – Loss of C in form of CH_4, CO, CO_2 at 300-1000 ºC

- Microscopic FTIR established qualitative *concentration* of B-C bonds

- Successful B-doping of monoliths with $B_{10}H_{14}$. Anisotropic liquid-gas reservoir:
  – B-conc. gradient from liquid side: 5.8%/cm
  – B-conc. gradient from gas side: 4.4%/cm

- Top undoped monoliths to date: 2200 m^2/g surface area; 4.3 µg/m^2 AEA

- Temperature evolution during charging of undoped 3.5" monolith (RT):
  – ΔT = +0.3 ºC for ΔP = 35 bar
  – T returns to original temp. with time constant of 2 min & 0.2 ºC/h