

# Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

P. Pfeifer<sup>1</sup>, C. Wexler<sup>1</sup>, P. Yu<sup>1</sup>, J. Burrell<sup>1</sup>, G. Suppes<sup>2</sup>, F. Hawthorne<sup>1,3,4</sup>, S. Jalisatgi<sup>4</sup>, M. Lee<sup>3</sup>, D. Robertson<sup>3,5</sup>

<sup>1</sup>Dept. of Physics, <sup>2</sup>Dept. of Chemical Engineering, <sup>3</sup>Dept. of Chemistry,  
<sup>4</sup>Dept. of Radiology, <sup>5</sup>University of Missouri Research Reactor  
University of Missouri, Columbia, MO 65211

2013 DOE Hydrogen Program Annual Merit Review, May 13-17, 2013

Project ID #ST19

This presentation does not contain any proprietary, confidential, or otherwise restricted information



# 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

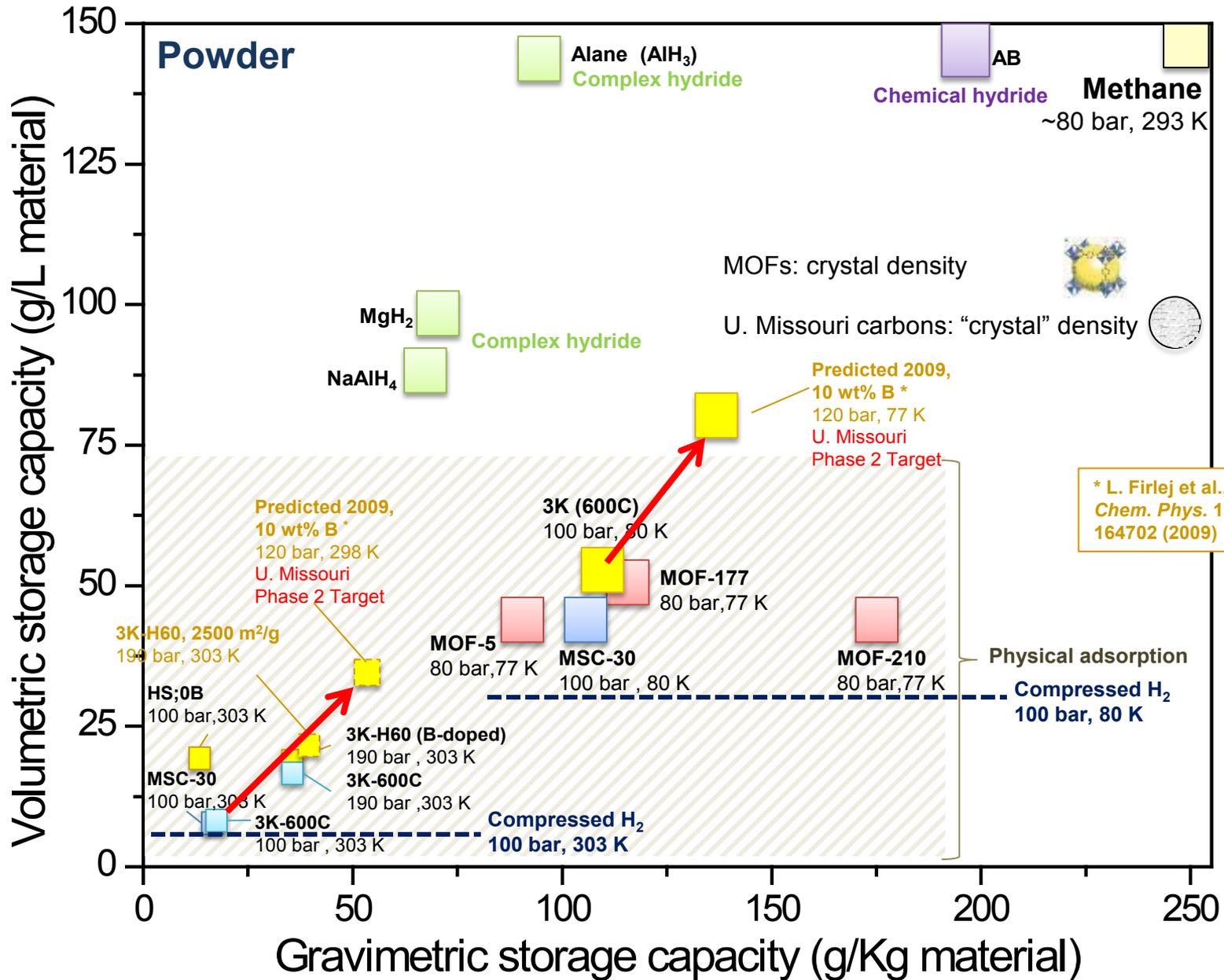
## Fabricate boron-doped monolithic nanoporous carbon for high-capacity reversible hydrogen storage (March 2012-March 2013)

- 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  $\sim 2700 \text{ m}^2/\text{g}$ , binding energies 10-15 kJ/mol, volumetric storage capacity  $>40 \text{ g/L}$  (material), and gravimetric storage capacity  $>5.5 \text{ wt\%}$  (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 ( $\text{sp}^2$  B-C bonds; FTIR, XPS)
- Establish enhanced binding energy and  $\text{H}_2$  adsorption on B-doped materials
- Determine  $\text{H}_2$  sorption kinetics and temperature evolution during charging/discharging of monoliths

# Relevance: Sorption Landscape



# Approach

Phase 2 Tasks	Milestones
<b>4—Manufacture, characterize, and optimize B-doped monoliths</b>	
<b>4.1—Optimize B-doping of best U. Missouri carbon powder in region 0-20 wt% B:(B+C)</b>	FY 2013 <ul style="list-style-type: none"> <li>• Protocol for optimum B-doping path; lowest B:C above which further B does not improve H<sub>2</sub> adsorption</li> <li>• Establish B-doped carbon powders with <math>\Delta H &gt; 12</math> kJ/mol, and boron conc. <math>&gt;10</math> wt%, completely substituted within carbon lattice</li> </ul>
<b>4.2—B-dope current U. Missouri monoliths and characterize H<sub>2</sub> storage</b>	FY 2013 <ul style="list-style-type: none"> <li>• Establish uniform B-concentration in doped monoliths and that boron is completely substituted in carbon lattice</li> <li>• Establish that performance of doped monoliths is comparable to doped powders</li> </ul>
<b>4.3—B-dope alternate powder precursors and respective monoliths</b>	FY 2014 Establish that Task 4.1/4.2-doped materials are superior to alternate doped materials
<b>4.4—Measure H<sub>2</sub> storage and kinetics on B-doped monoliths in 0.5-liter H<sub>2</sub> Test Fixture at 295 K and on Sievert apparatus at 77 K</b>	FY 2014 <ol style="list-style-type: none"> <li>1. Establish B-doped monoliths with <math>\Sigma \sim 2700</math> m<sup>2</sup>/g, <math>\Delta H = 10-15</math> kJ/mol, gravimetric storage capacity <math>&gt;5.5</math> wt% (material), volumetric storage capacity <math>&gt;40</math> g/L, at 100 bar &amp; 295 K</li> <li>2. Establish B-doped monoliths with <math>\Sigma \sim 2700</math> m<sup>2</sup>/g, <math>\Delta H = 10-15</math> kJ/mol, gravimetric storage capacity <math>&gt;12</math> wt%</li> </ol>

# Technical Accomplishments

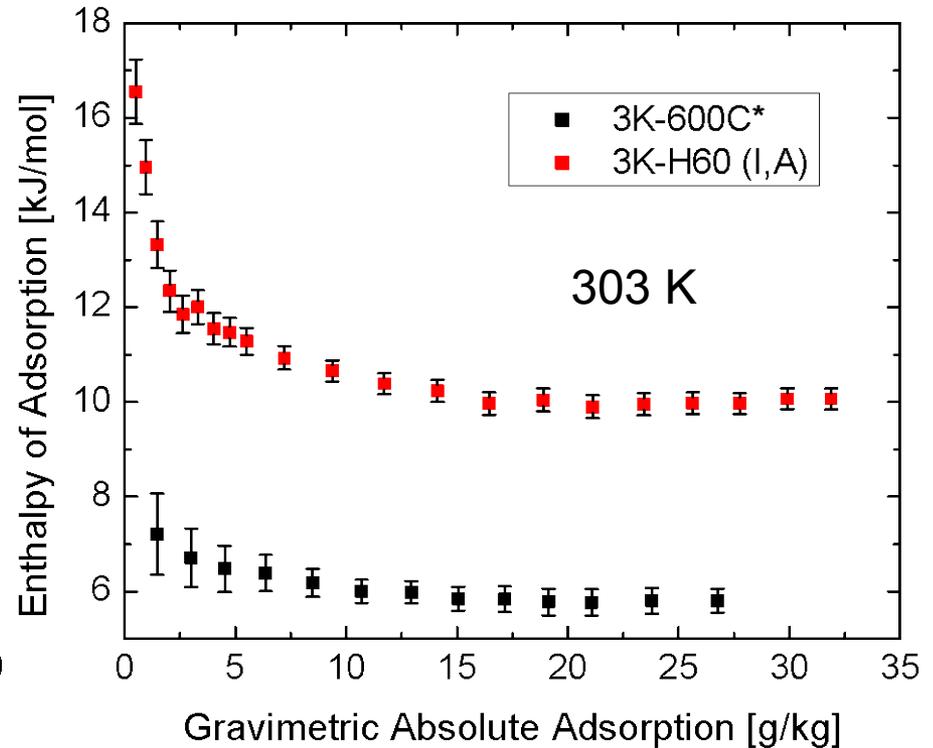
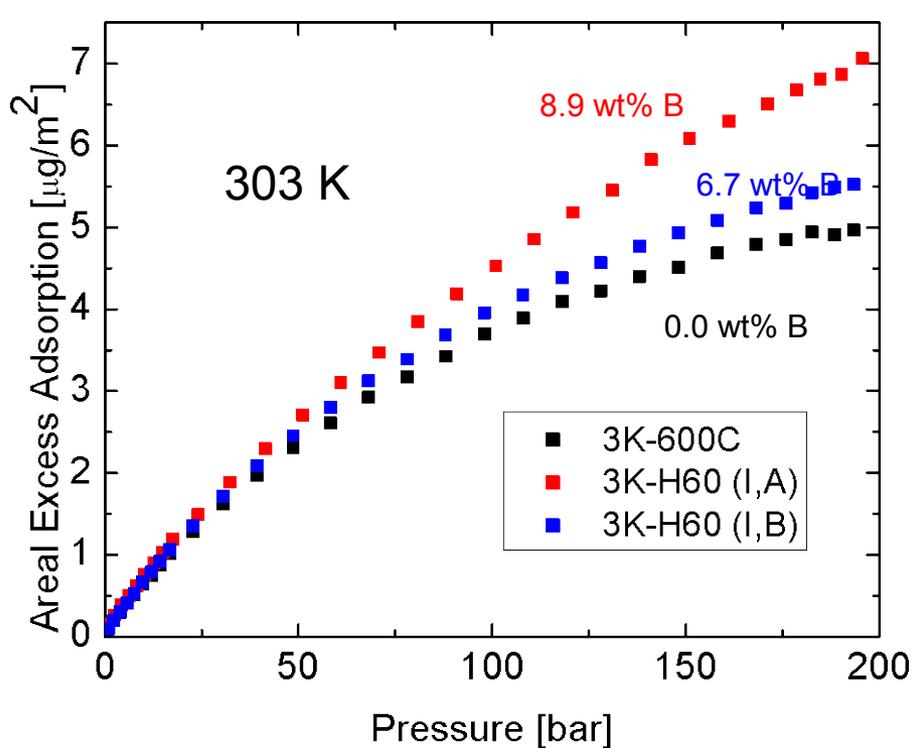
## Best Performing Carbons

	Max. Grav. Excess (wt. % material)	Gravimetric Storage (wt. %, material)	Volumetric Storage (g/L material)	Surface Area (m <sup>2</sup> /g)	Isosteric Heat (kJ/mol)
3K-600C, <b>80 K</b> , 200 bar	6.3 (60 bar)	<b>12.0</b>	<b>63</b>	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	<b>9.5</b>	2,100	-
3K-120C, <b>1.5 kg tank</b> , 296 K, 100 bar	0.80	<b>3.0</b>	8.8	2,600	-
3K-H60 (I,A), <b>B:C = 8.9%</b> 303 K, 200 bar	1.5	<b>3.4</b>	<b>18</b>	2,100	<b>Zero coverage: 17 High coverage: 10</b>
Predicted 2009 <b>(B:C = 10%</b> , 2600 m <sup>2</sup> /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

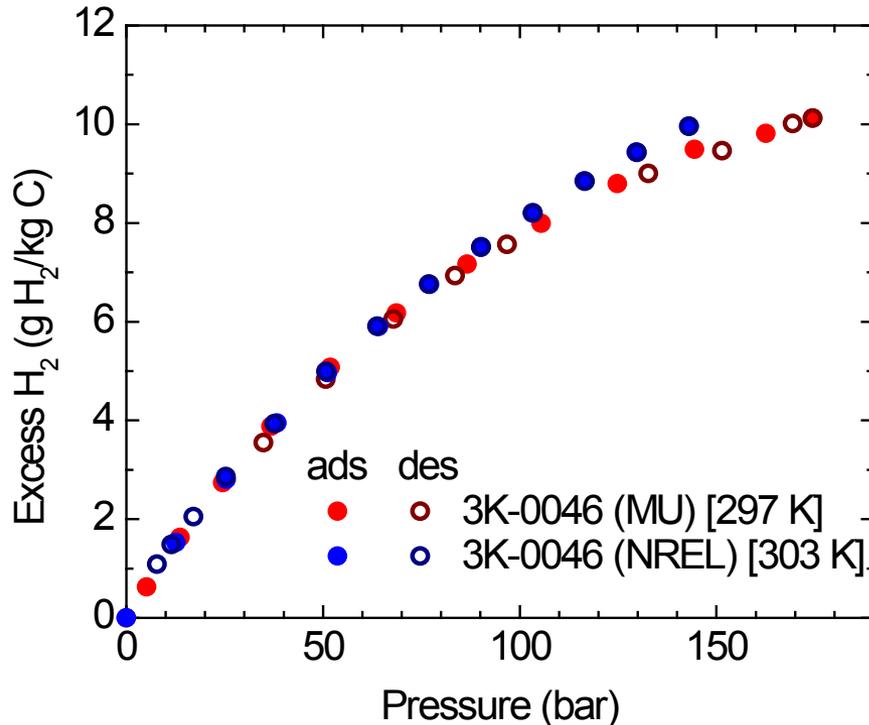


- $\text{H}_2$  excess adsorption per unit surface area (areal excess adsorption, AEA) depends only on how strongly surface binds  $\text{H}_2$ , not on surface area or pore volume. 40% increase in AEA at 200 bar: high binding energies on majority of surface sites
- Enthalpy of adsorption,  $\Delta H$ , increased from 6 kJ/mol (0.0 wt% B) to 10 kJ/mol (8.9 wt% B)
- Film thickness  $t$  from  $\Delta H$  analysis:  $t = 0.6$  nm at 303 K (AMR 2010:  $t = 0.4$  nm at 77 K)
- Task: Reproduce B-doped sample & high  $\Delta H$ ; validate at NREL

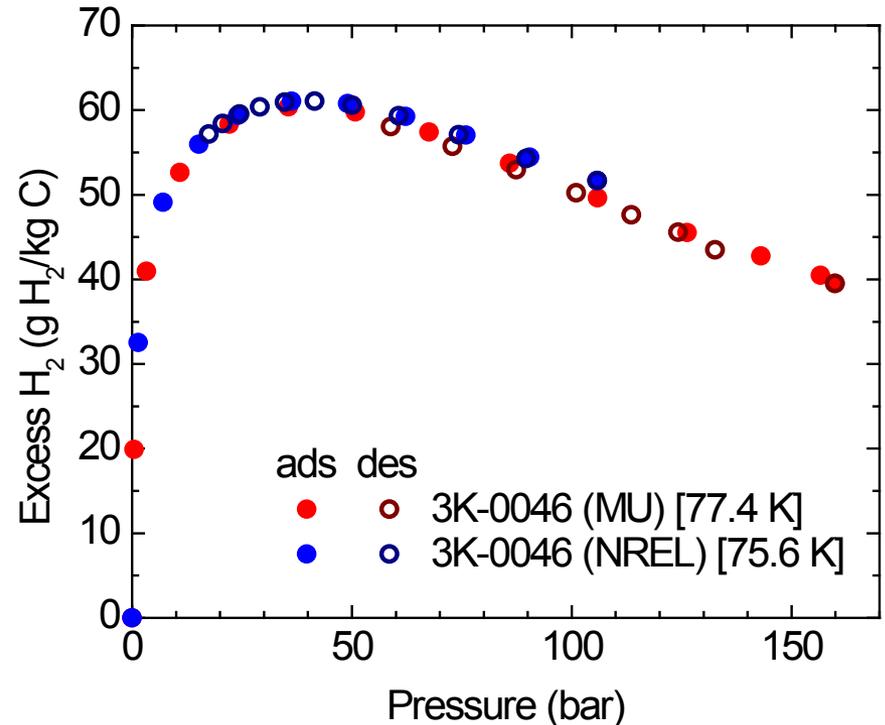
# Technical Accomplishments

New U. Missouri undoped carbon: 3K-0046

Room temperature



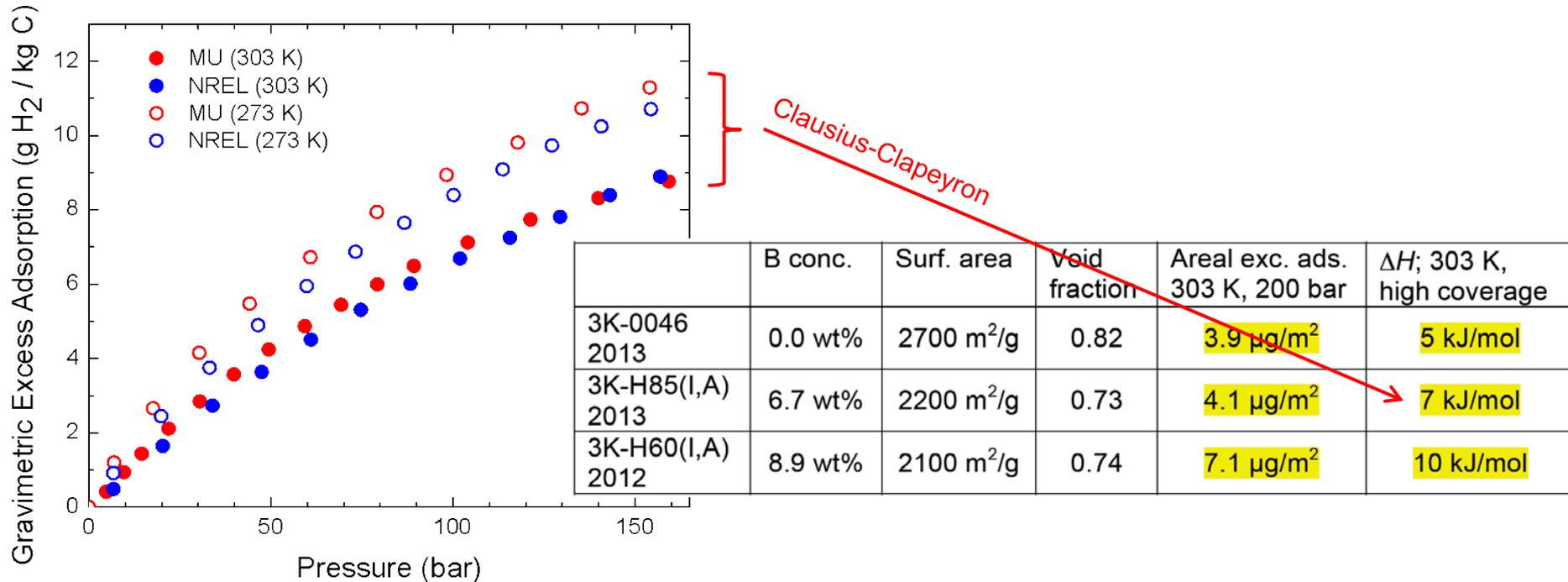
Liquid nitrogen (LN<sub>2</sub>) temp.



- Room temperature and LN<sub>2</sub> isotherms (adsorption and desorption) at NREL and U. Missouri agree; measured on same aliquot
- U. Missouri utilized LN<sub>2</sub> bath, replicating LN<sub>2</sub> bath at NREL
- Difference in LN<sub>2</sub> boiling temperature due to difference in elevation

# Technical Accomplishments

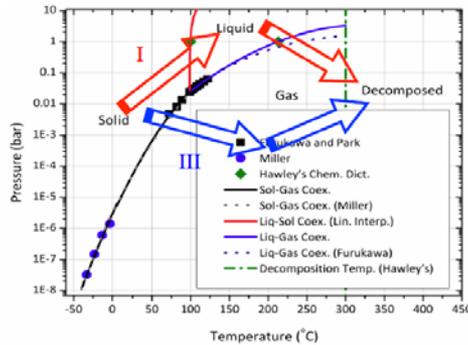
New U. Missouri B-doped carbon: 3K-H85(I,A), 6.7 wt% B



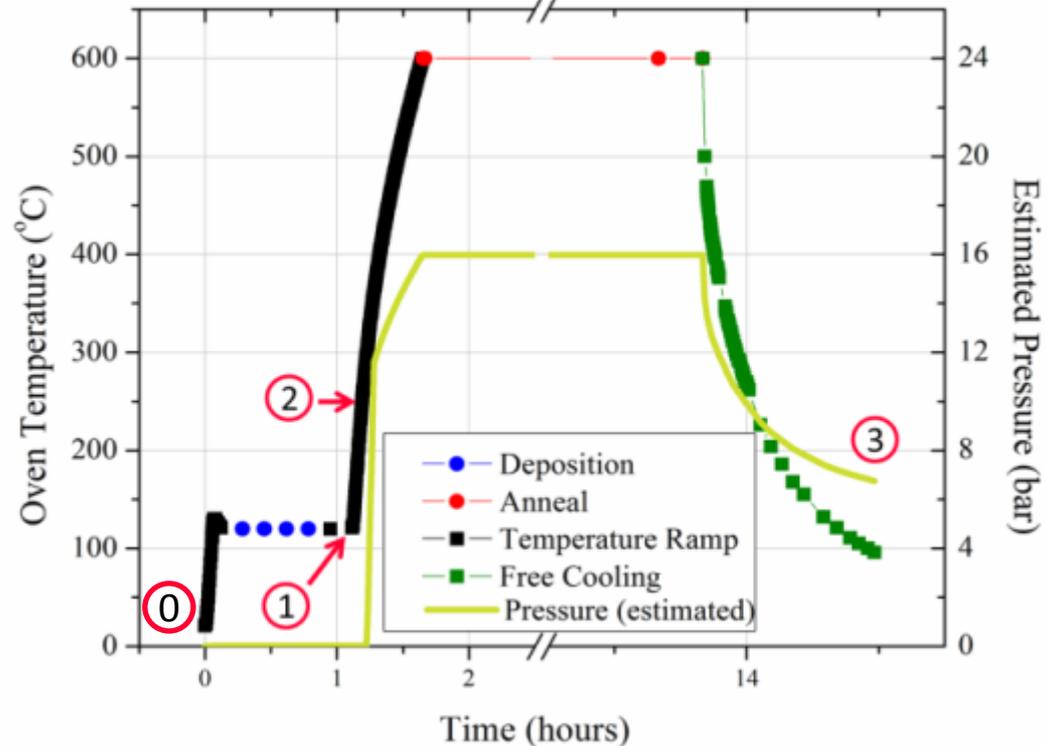
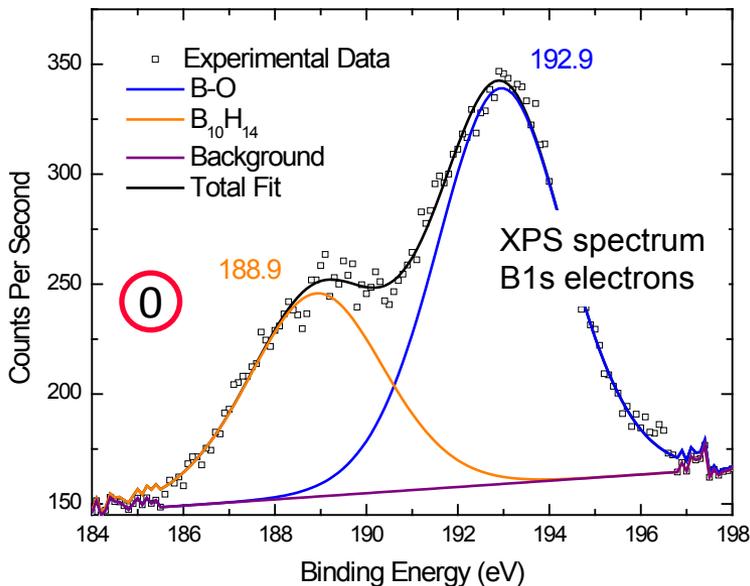
- 30 °C and 0 °C isotherms at NREL and U. Missouri agree
- Reproduced: B-doping/annealing (600 °C) reduces surface area by <20%
- Reproduced: Both AEA and  $\Delta H$  increase with increasing B concentration
- AEA,  $\Delta H$  increase nonlinearly: largest increase from 6.7 to 8.9 wt% B
- 3K-H85(I,A):  $\Delta H$  increased from 5 kJ/mol (0.0 wt% B) to 7 kJ/mol (6.7 wt% B)
- 3K-H60(I,A):  $\Delta H$  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<sup>-</sup> anions

# Technical Accomplishments

## B-doping monitored by x-ray photoelectron spectroscopy (XPS)



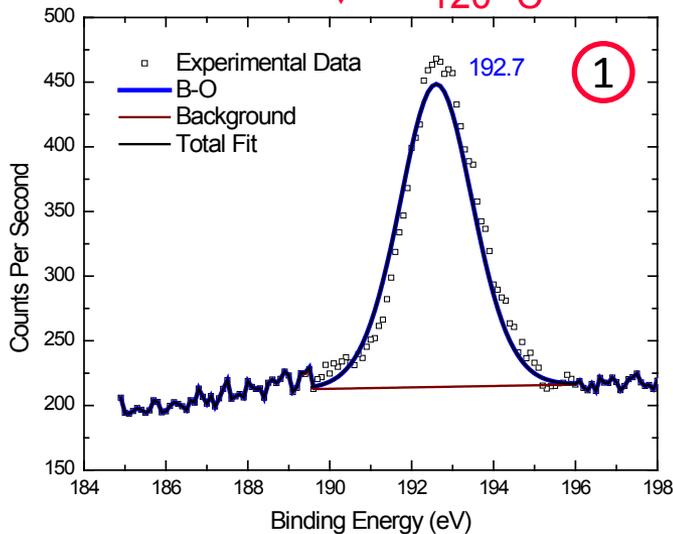
0. Decaborane/carbon mixture
1. Decaborane is deposited, but has not reacted
2. Decaborane reacts/decomposes
3. After annealing at 600 °C: 3K-H89(I,A), 8.6 wt% B



- 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

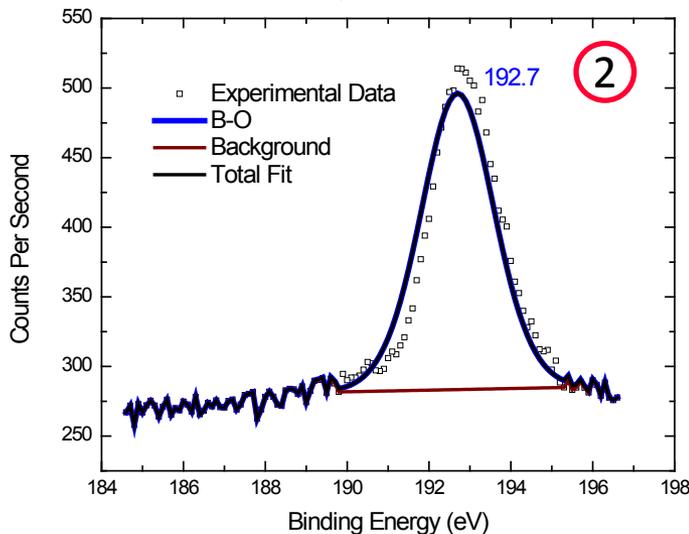
# Technical Accomplishments

↓ Deposition at  
120 °C



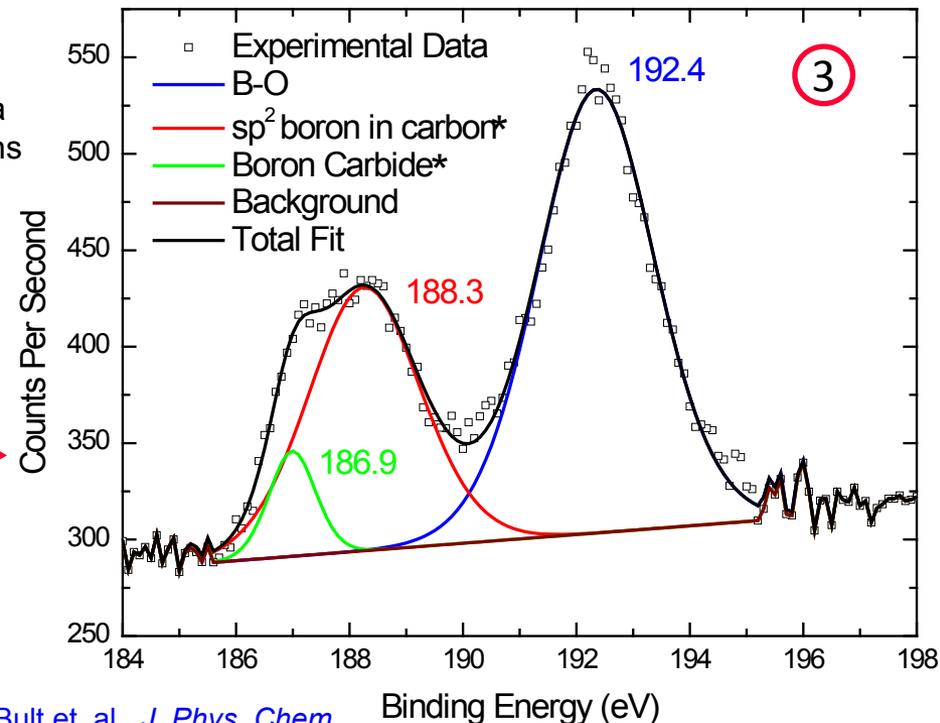
- 120 °C, no B<sub>10</sub>H<sub>14</sub>: B<sub>10</sub>H<sub>14</sub> evaporated in XPS UHV chamber
- 250 °C, no B-C or B-B peak: B<sub>10</sub>H<sub>14</sub> has not decomposed yet
- Final material, 3K-H89(I,A), 8.6 wt% B:
  - 188 eV peak: sp<sup>2</sup> B-C bonds [\*]; enhanced binding of H<sub>2</sub>
  - 187 eV peak: B<sub>4</sub>C B-C bonds [\*]; unenhanced binding of H<sub>2</sub>
  - 6 out of 7 B-C bonds are sp<sup>2</sup> bonds
  - B-B bonds: may be present, but buried under B-C peaks
  - 192 eV peak: B-O bonds survive at 600 °C (undesirable)

↓ At 250 °C



XPS spectra  
B1s electrons

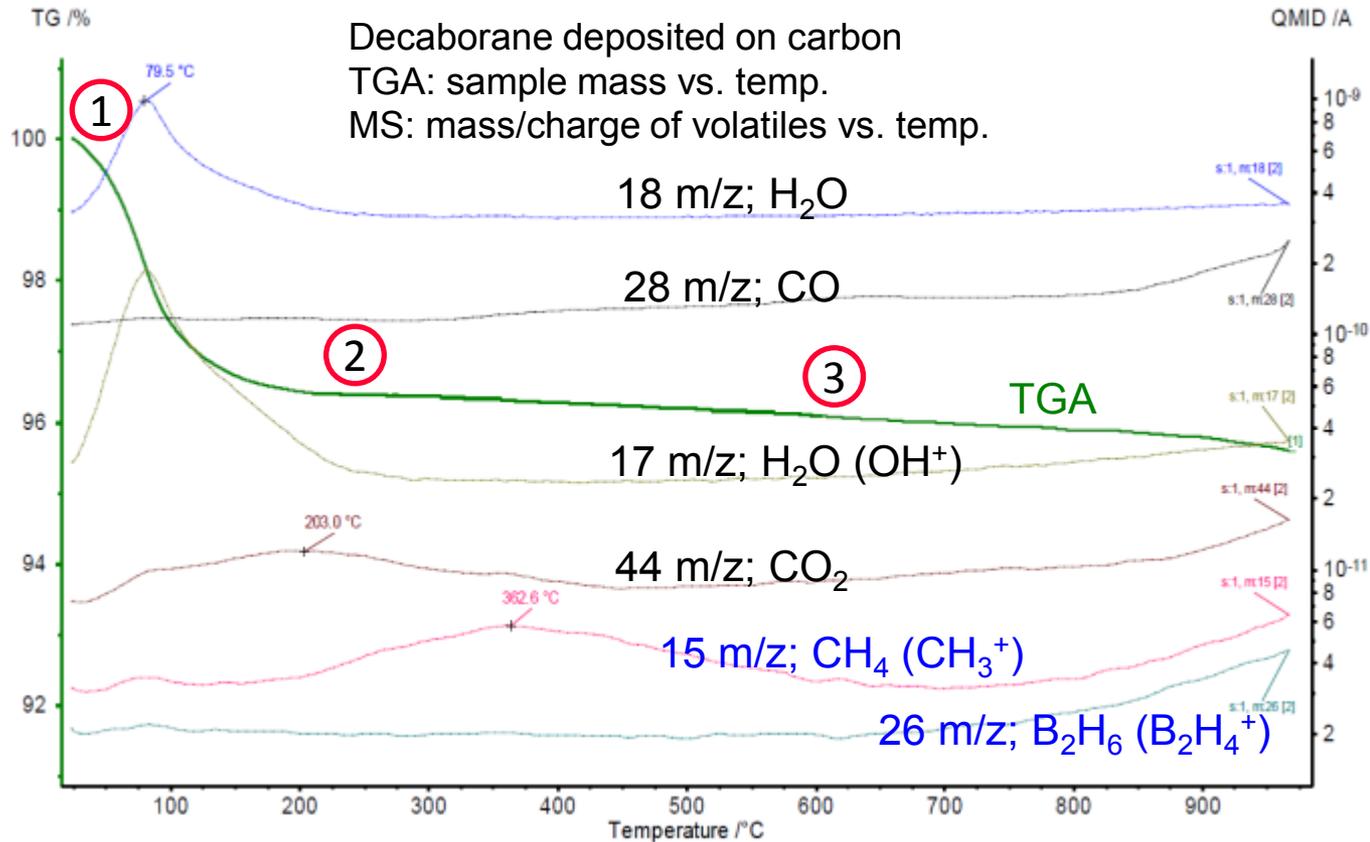
→ Anneal at  
600 °C



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

# Technical Accomplishments

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

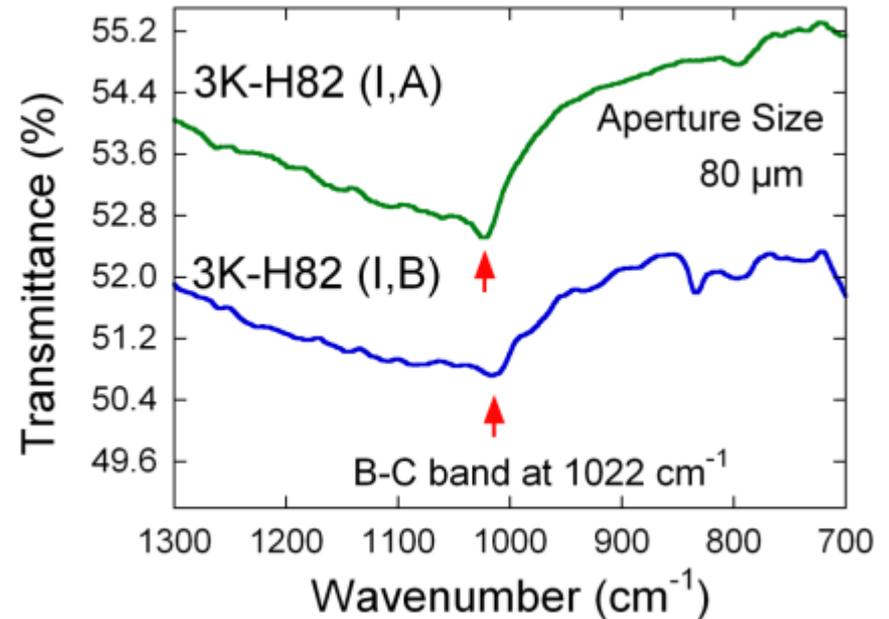
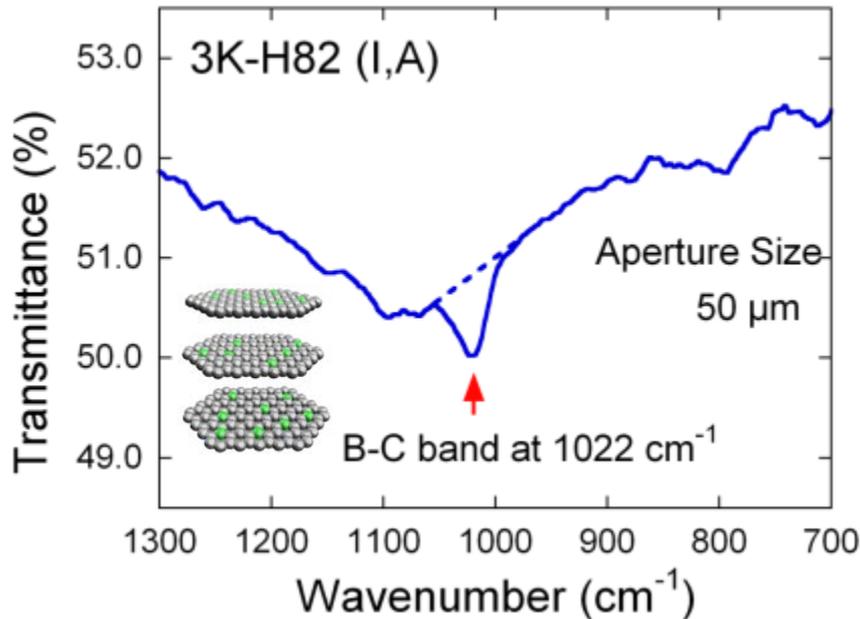


- H<sub>2</sub>O, CO, CO<sub>2</sub>: from sample exposure to air & removal of surface-bound oxygen
- 350 °C: CH<sub>4</sub> from decomposition of B<sub>10</sub>H<sub>14</sub> on C
- 600-1000 °C: boron loss in form of B<sub>2</sub>H<sub>6</sub>
- Boron loss, from 8.9 to 6.7 wt%, at 600-1000 °C, observed previously by PGAA
- Rise of CO, CO<sub>2</sub> at >600 °C: removal of surface-O requires >600 °C, also on B-free carbons

# 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 °C	6.7
3K-H82(I,B): annealed at 1000 °C	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

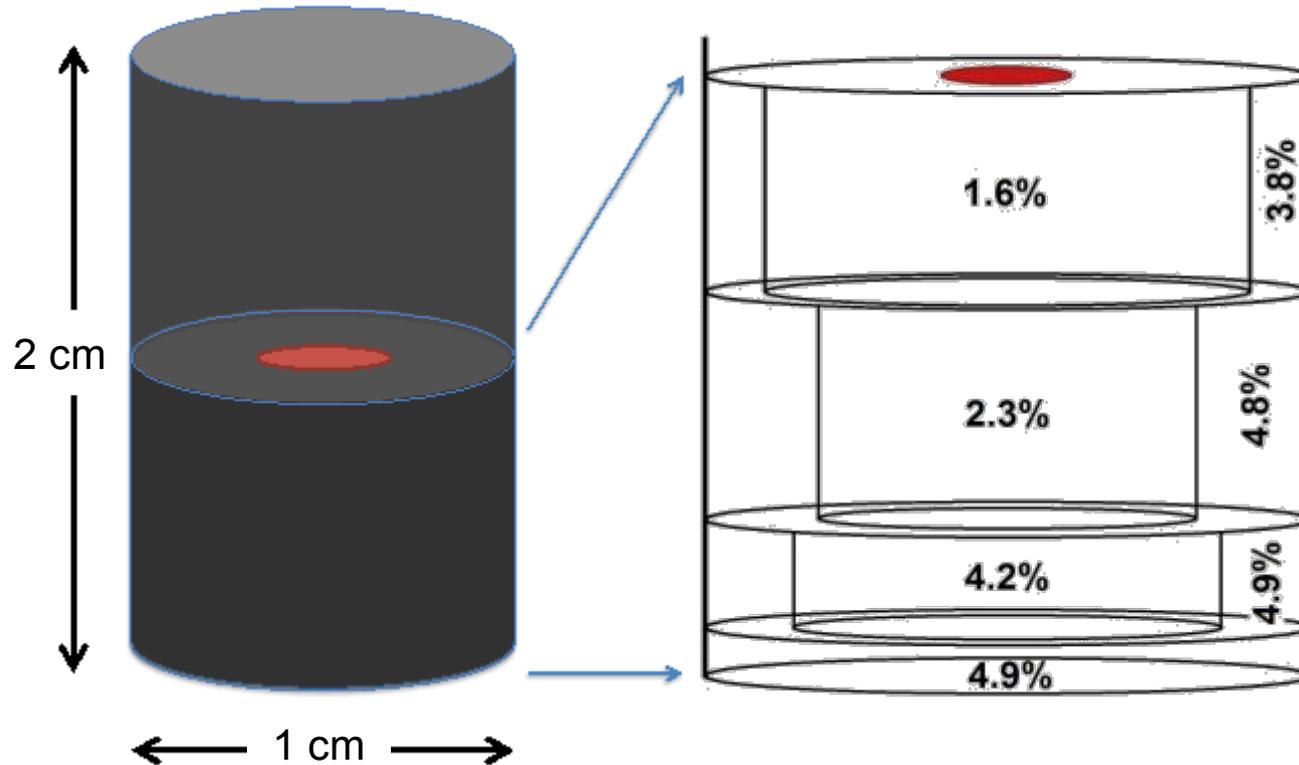
# Technical Accomplishments

## 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<sub>2</sub> binding energies
- Objective 2: Dope monoliths with 0-20 wt% B, for high H<sub>2</sub> binding energy
- Objective 3: Determine H<sub>2</sub> 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<sub>10</sub>H<sub>14</sub>. Alternative—first B-dope powder, then fabricate monoliths—not pursued
- Achieved: B<sub>10</sub>H<sub>14</sub> 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

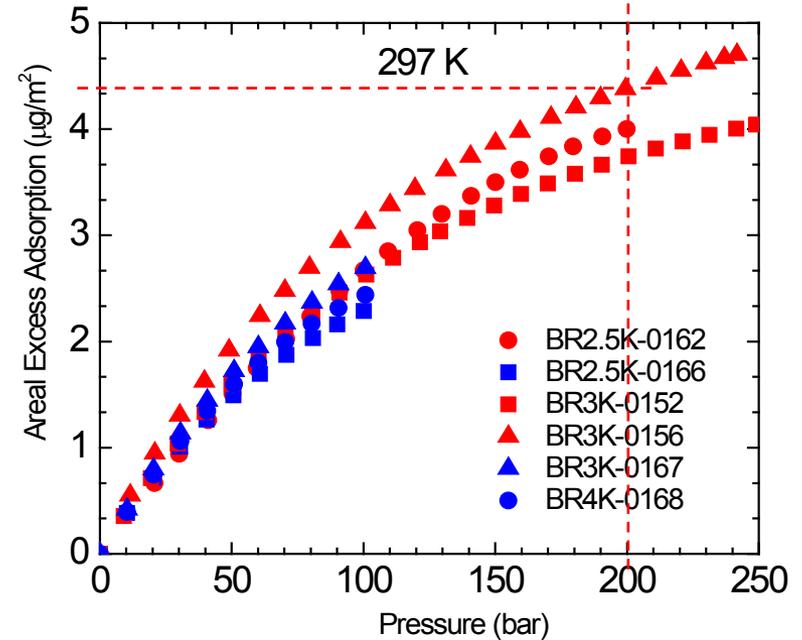
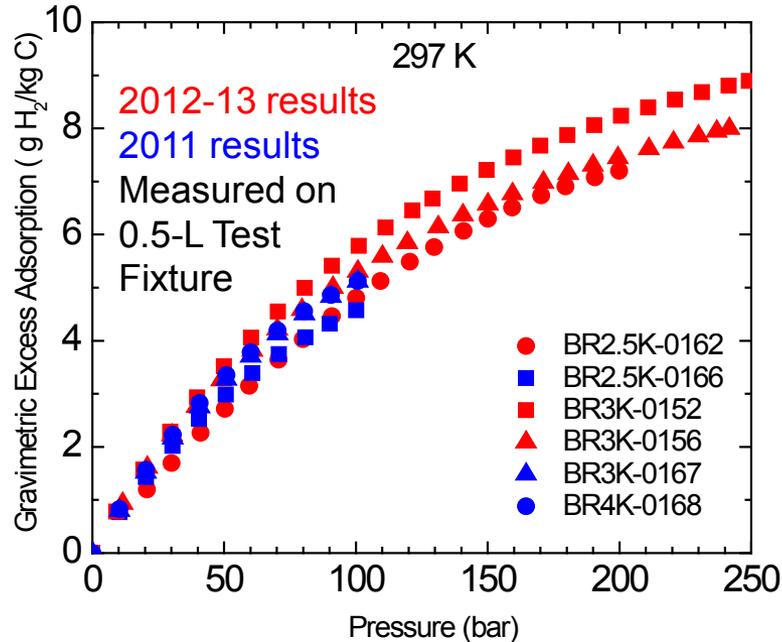
## Spatial distribution of boron in doped monoliths



- 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  $(r, z) = (0 \text{ cm}, 0.25 \text{ cm})$ : **successful doping from liquid phase**
- **3.8 wt% B** at  $(r, z) = (0.45 \text{ cm}, 0.85 \text{ cm})$ : **successful doping from gas phase**
- Drop from 3.8 to 1.6 wt% B at  $z = 0.85 \text{ cm}$ : **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  $r = 0 \text{ cm}$ : **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<sub>2</sub> performance



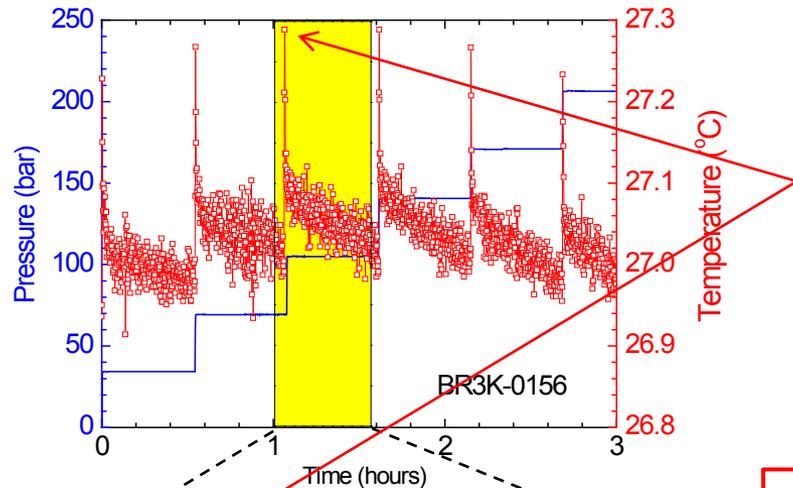
	Binder: carbon (wt)	Compaction temp.	Pyrolysis temp.	Surface area	Porosity (N <sub>2</sub> )
BR2.5K-0162	1.25	230 °C	750 °C	1800 m <sup>2</sup> /g	0.66
BR3K-0152	1.00	280 °C	750 °C	2200 m <sup>2</sup> /g	0.73
BR3K-0156	1.00	170 °C	850 °C	1700 m <sup>2</sup> /g	0.67



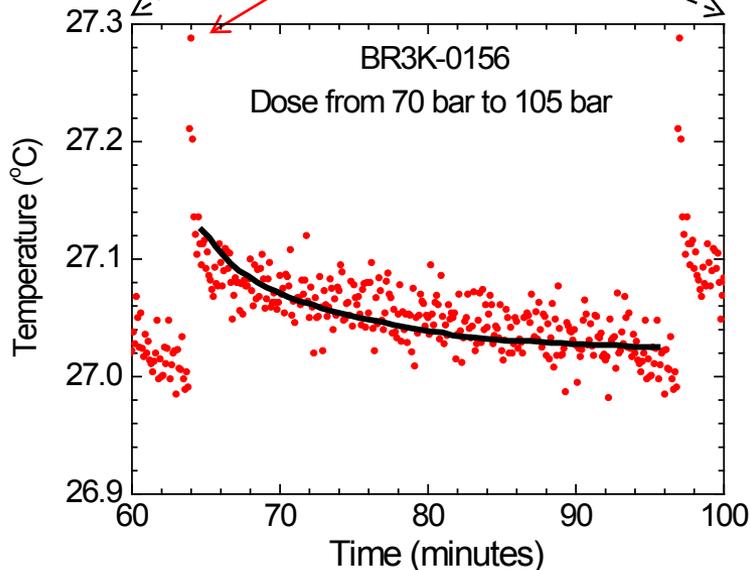
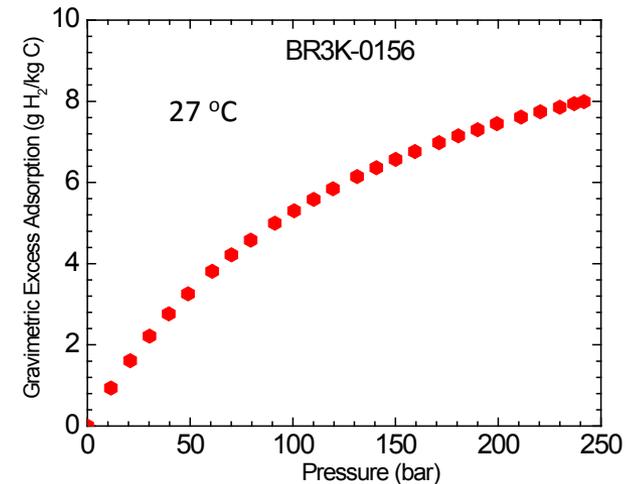
- Compaction at 230 °C favors lower porosity, thus high volumetric storage capacity
- BR3K-0152: high gravimetric excess adsorption due to high surface area; but low areal excess adsorption (AEA) due to abundance of supra-nm pores
- BR3K-0156: **high AEA (high binding energy)** due to dominance of sub-nm pores  
AEA at 200 bar and room temp.: **4.3 µg/m<sup>2</sup>—higher than B-doped powder 3K-H85(I,A)**

# Technical Accomplishments

Kinetics on undoped 3.5" monolith: charging/discharging rates, thermal management



Heating due to adiabatic compression and heat of adsorption



- 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 °C**
- Excursion largest at 0-150 bar (heat of adsorption large when H<sub>2</sub> uptake large: low pressure)
- Temperature drops, from maximum (27.3 °C), **first exponentially with time constant of 2 min, then linearly at 0.2 °C/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<sub>2</sub> 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<sub>2</sub>
- **U. Montpellier II & U. Marseille**, France (Academic): L. Firlej & B. Kuchta—GCMC simulations
- **Wroclaw U. Technology**, Poland (Academic): S. Roszak—adsorption potentials for H<sub>2</sub> 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<sub>2</sub>
- **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 °C)
  - Suppress conversion of B• free radicals into B<sup>-</sup> anions; test B-doped materials for free radicals by electron paramagnetic resonance spectroscopy (EPR); determine XPS and FTIR spectra of anionic sp<sup>2</sup> B<sup>-</sup>-C bonds on model compound; estimate H<sub>2</sub> binding energy on B<sup>-</sup>-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,  $\Delta H$ , and areal excess adsorption for H<sub>2</sub>, at 77 K and 273 K, on B-doped powders with 0-20 wt% B. Improve determination of  $\Delta H$  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  $\Delta H$  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:  $\Delta H$  increased from 6 to 10 kJ/mol; AEA increased by 40%  
3K-H85(I,A), 6.7% wt% B:  $\Delta H$  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<sup>2</sup>/g  
Top AEA's to date (RT, 200 bar): 3.9, 4.1, 7.1  $\mu\text{g}/\text{m}^2$
- XPS established two types of B-C bonds: (a) sp<sup>2</sup> bonds (90%, enhance H<sub>2</sub> binding);  
(b) B<sub>4</sub>C bonds (10%, do not enhance H<sub>2</sub> binding)
- XPS, TGA-MS, and PGAA established:
  - Presence of B-O bonds (inert up to 600 °C)
  - Loss of B in form of B<sub>2</sub>H<sub>6</sub> at 600-1000 °C (20-30% loss)
  - Loss of C in form of CH<sub>4</sub>, CO, CO<sub>2</sub> at 300-1000 °C
- Microscopic FTIR established qualitative *concentration* of B-C bonds
- Successful B-doping of monoliths with B<sub>10</sub>H<sub>14</sub>. 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<sup>2</sup>/g surface area; 4.3  $\mu\text{g}/\text{m}^2$  AEA
- Temperature evolution during charging of undoped 3.5" monolith (RT):
  - $\Delta T = +0.3$  °C for  $\Delta P = 35$  bar
  - $T$  returns to original temp. with time constant of 2 min & 0.2 °C/h