

Discovery of Materials with a Practical Heat of H₂ Adsorption

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May 22, 2009

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Overview

Timeline

- Project start date: 3/1/05
- Project end date: 2/28/10
- ~90% complete

Budget

- Total project \$3,948,220
 - DOE share \$3,158,575 (80%)
- FY08 funding \$700,000
- FY09 funding \$750,000

Partners

- Current collaborations: Penn State, Texas A&M University
- Anticipated/other interactions: NREL, Rice University, Univ. of Michigan (coordination of computational modeling efforts)

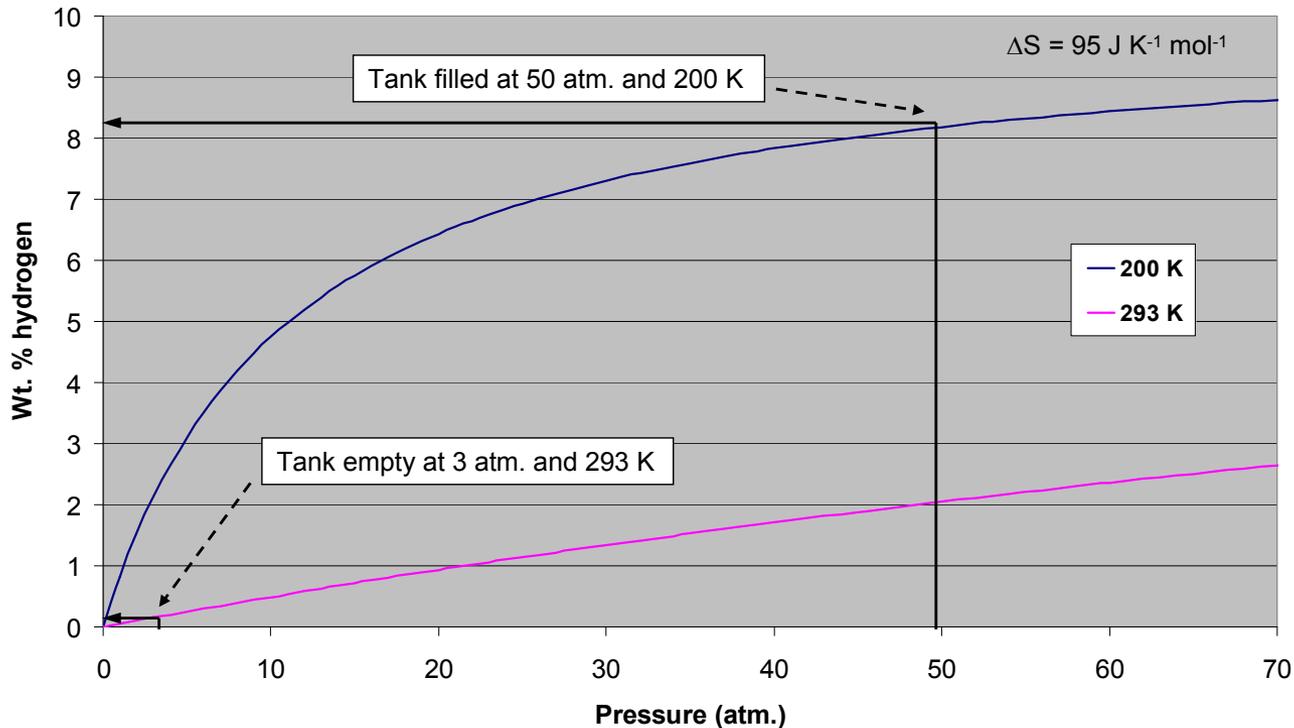
Barriers

- Technical Barriers- Hydrogen Storage
 - A. System Weight and Volume
 - C. Efficiency
 - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Relevance – Project Objectives

- Development and testing of new materials with high H₂ storage density and appropriate enthalpy of hydrogen adsorption for operation of hydrogen storage systems at practical engineering pressures and temperatures:
 - This task addresses H₂ Storage Technical Barriers A (System Weight and Volume) and C (Efficiency)
 - Leverages our existing materials science and chemistry capabilities (eg. fluorine chemistry) to generate new hydrogen storage materials for testing
- Development of enabling technologies for H₂ storage materials development by HSCoE partners:
 - This task addresses H₂ Storage Technical Barrier P (Lack of Understanding of Hydrogen Physisorption and Chemisorption)
 - Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding of hydrogen spillover
 - Development of unique characterization tools for accurate H₂ storage measurements
 - Measurement of hydrogen isotherms for HSCoE partners (~25% of available instrument time)

Relevance – Enhanced Physisorption



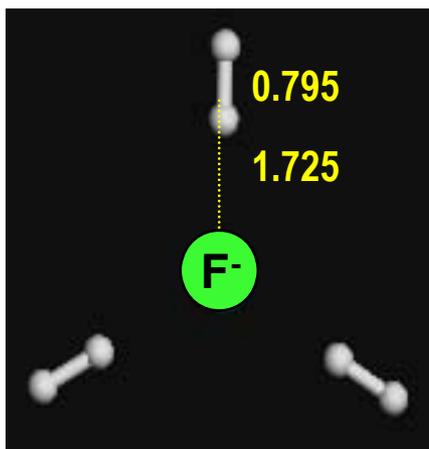
Simulated Langmuir isotherms at 200 and 293 K for an adsorbent with $\Delta H = 15 \text{ kJ/mol}$ (assumptions: maximum capacity = 10 wt. %, $\Delta S = 95 \text{ J K}^{-1} \text{ mol}^{-1}$)

Physisorption of H_2 using materials with a practical enthalpy can enable hydrogen storage systems that operate at moderate pressures and temperatures

Approach – Technical Motivation

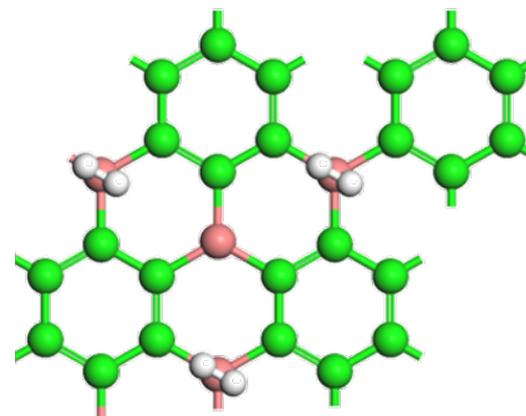
- How can we enable and execute discovery of materials with enhanced enthalpy relative to “conventional” hydrogen storage materials (eg. activated carbon)?
 - Interaction of hydrogen with either electron-deficient species (electrophiles, Lewis acids) or very strong electron donors (Lewis bases)

Interaction of H₂ with a fluoride anion



$$\Delta E = -24.3 \text{ kJ/mol H}_2$$

Adsorption of H₂ on boron atoms of BC₃



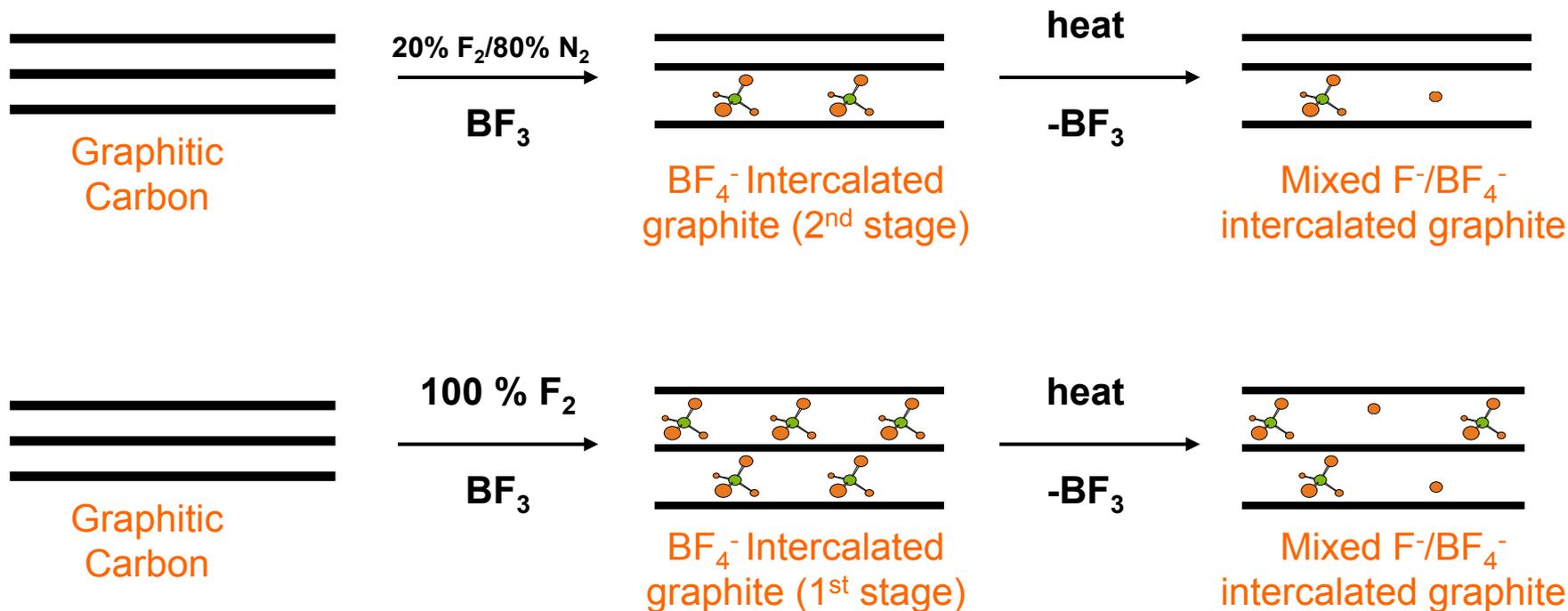
Approach – Discovery of New H₂ Storage Materials

- Translate predictive computational modeling to development and testing of new H₂ storage materials
 - Novel materials development based upon theoretical predictions of high H₂ storage density and/or enthalpy
 - Materials synthesis (fluorine chemistry, novel boron-containing carbon materials)
- General quantitative computational models for new materials discovery
 - Through collaborative efforts within the CoE, realize a more practical overlap between computational and experimental work (e.g., modeling mechanism of hydrogen spillover)
- Accurate measurement techniques
 - Correction for helium adsorption effects on H₂ isotherms
 - Surface area determination using H₂ condensation as a more informative alternative to conventional N₂ sorption methods

Approach - Milestones

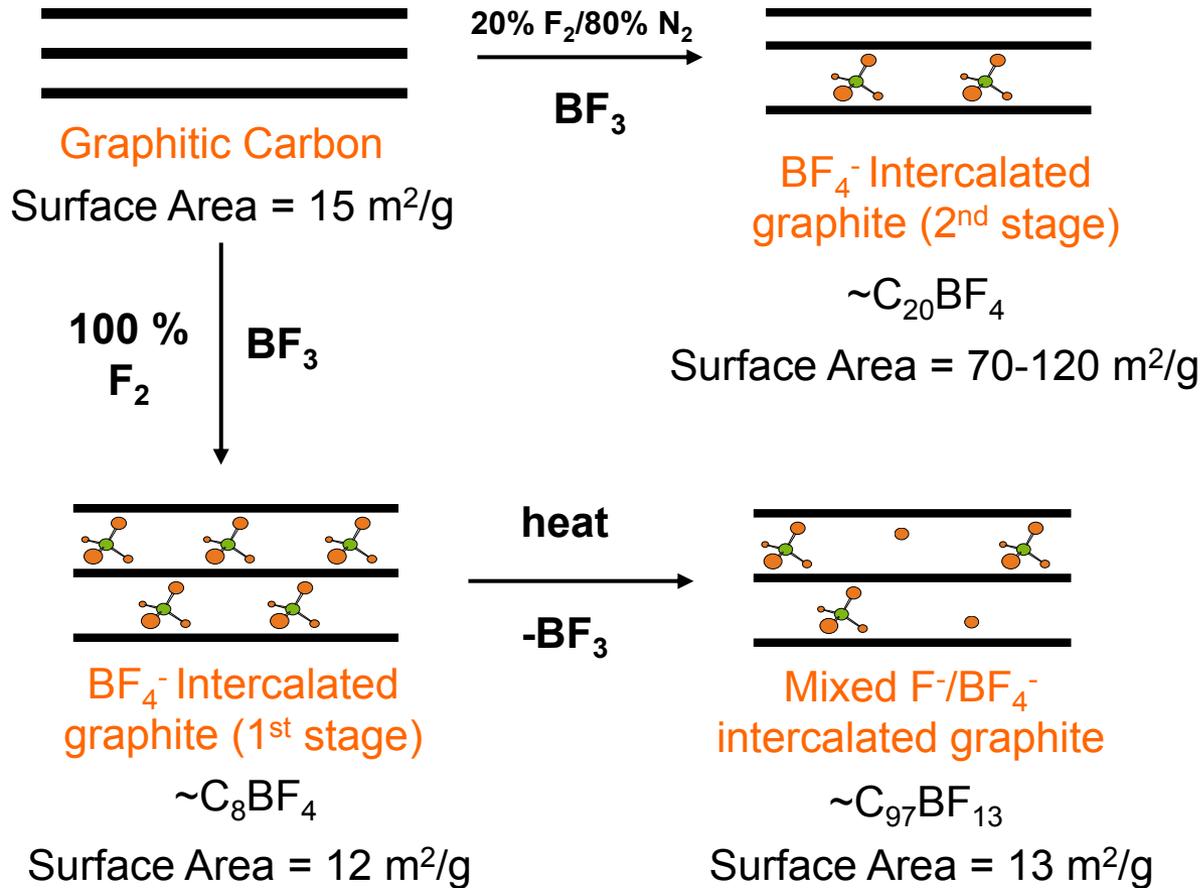
	Milestone
3QFY08	Finish <i>ab initio</i> MD simulations and minimum energy path calculations on BC_3 and related compounds
1QFY09	Find optimal BF_4^-/F^- ratios for maximum H_2 uptake and heat of adsorption in intercalated graphite
2QFY09	Go/no go decision on F^- intercalated graphite Identify synthetic routes to novel boron-containing carbon materials

Technical Accomplishments – Synthesis of F⁻/BF₄⁻ Graphite Intercalation Compounds (GIC)



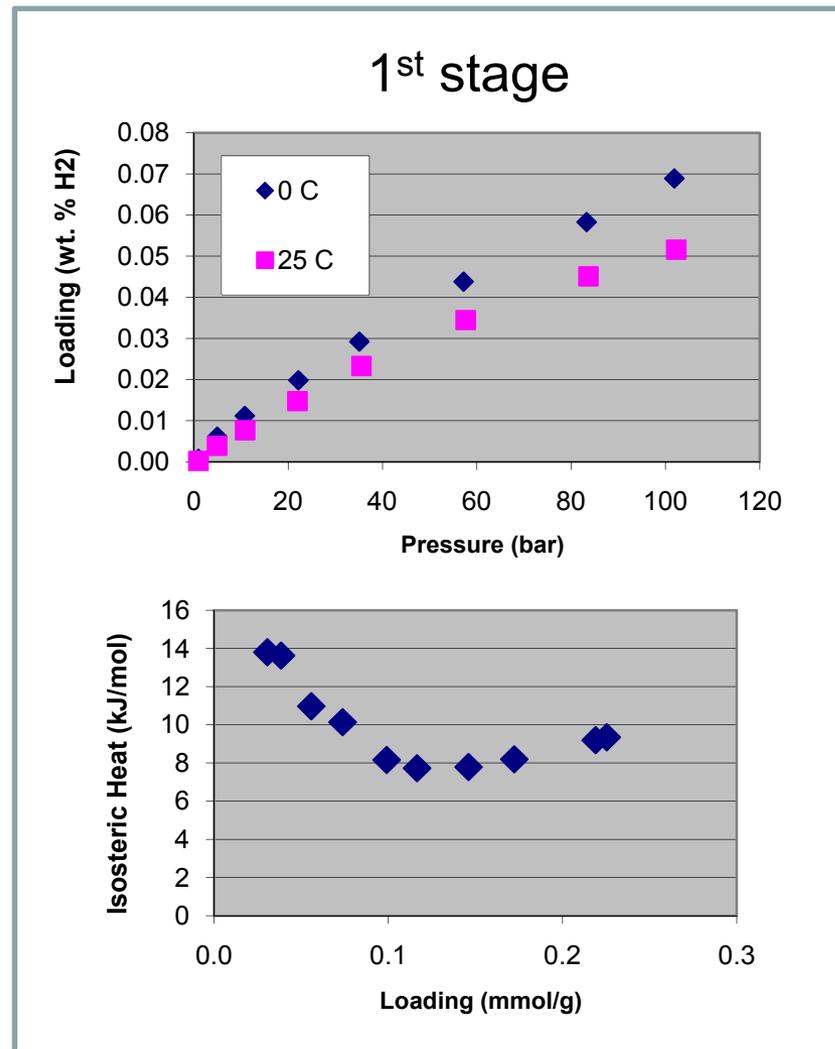
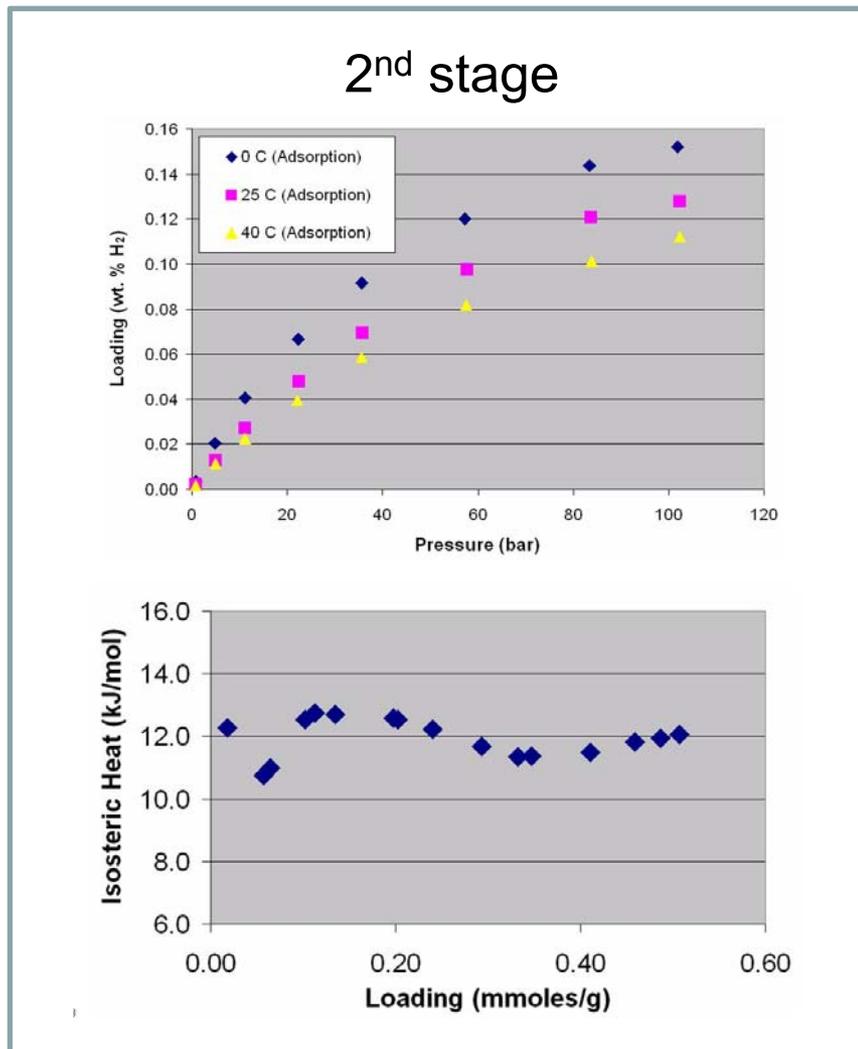
Our upgraded experimental procedure has facilitated the use of pure F₂ which allowed the synthesis of 1st stage BF₄⁻ intercalated graphite

Technical Accomplishments – Creation of Microporosity by Anion Intercalation



1st stage GIC shows no improvement in surface area

Technical Accomplishments – Comparison of H₂ isotherms on 1st and 2nd Stage Compounds



1st stage GIC shows higher initial heat, lower overall capacity

Technical Accomplishments – Synthesis and Testing of GIC's Prepared with High Surface Area Hosts

Carbon	S.A. (m ² /g)	Intercalant	Elemental Analysis	S.A. of GIC (m ² /g)	H ₂ capacity @ 25 °C, 100 bar	ΔH (kJ/mol H ₂)	
Graphite	15	BF ₄ ⁻	C ₂₅ BF ₄	75	0.12 wt. %	12	Change Anion
Graphite	15	HF ₂ ⁻	C _{3.4} F	18	0.04 wt. %	4.5	
Graphitized Activated Carbon	145	BF ₄ ⁻	C ₅₁ BF ₅	20.7	0.18 wt. %	7	Change Host Material
Activated C Fiber	1800	BF ₄ ⁻	C ₁₅₄ BF ₃₁	775	0.20 wt. %	7	
Activated Carbon (AX-21)	2500	BF ₄ ⁻	C ₁₂₃ BF ₈	2390	0.60 wt. %	7	

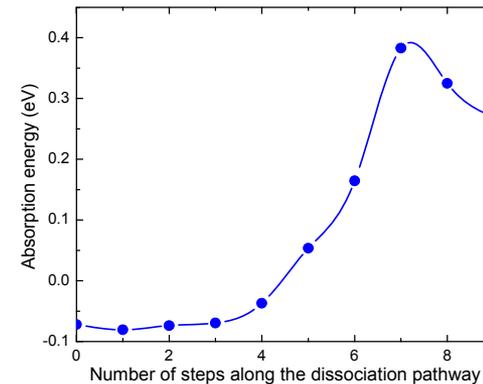
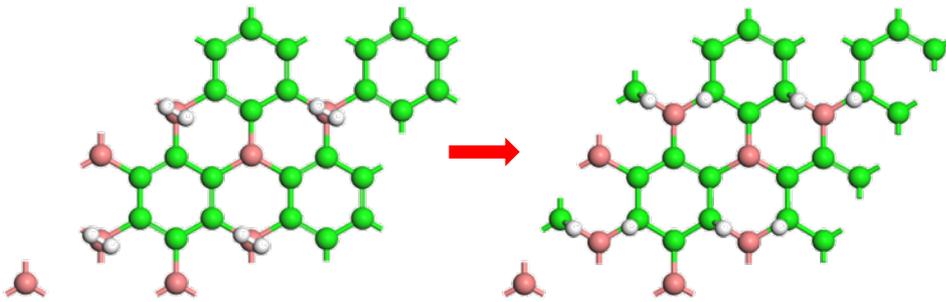
Elemental Analysis indicates low levels of intercalation and covalent C-F bond formation (fluorination)

Isosteric heat calculations indicate little enhancement of H₂ adsorption enthalpy relative to host materials

Background - Hydrogen Spillover in BC₃

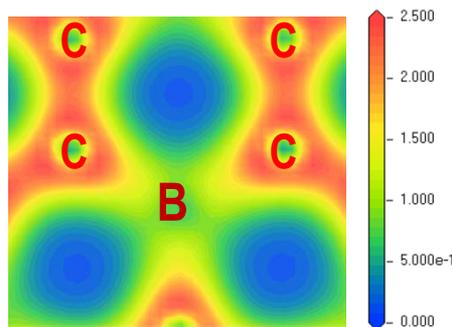
Published LDA calculations indicate that H₂ undergoes spontaneous dissociation in bulk BC₃
Zhang and Alavi (J. Chem. Phys. 2007, 127, 214704)

H₂ dissociative chemisorption on a BC₃ sheet:

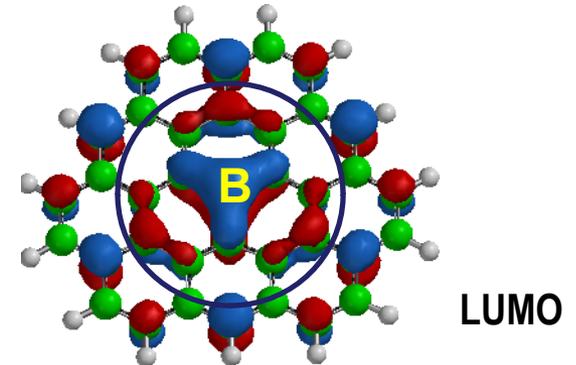
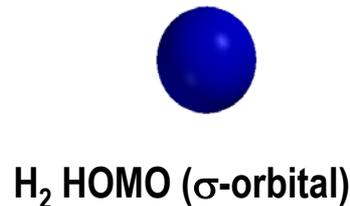


moderate barrier
endothermic reaction

Electron density:



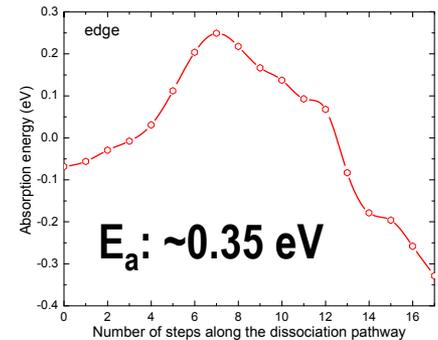
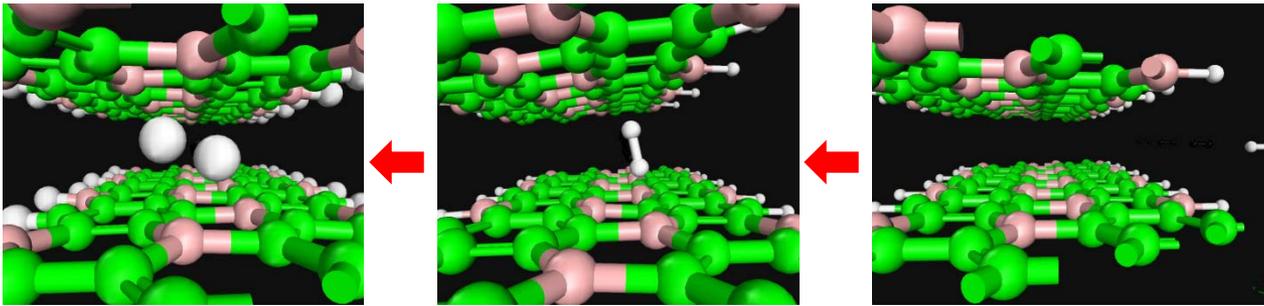
Orbital interaction:



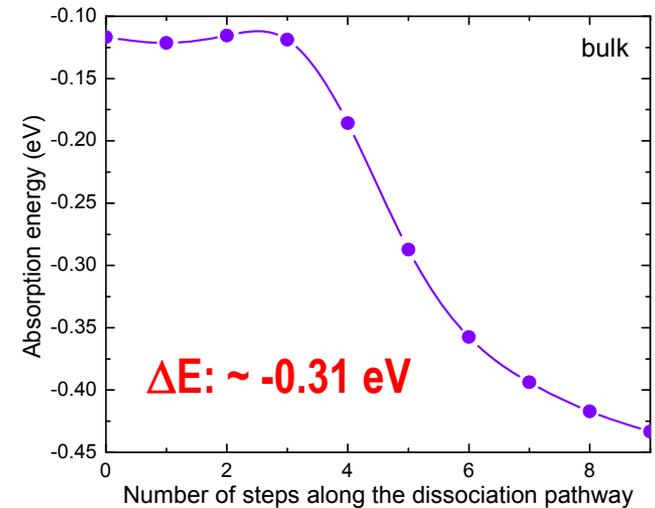
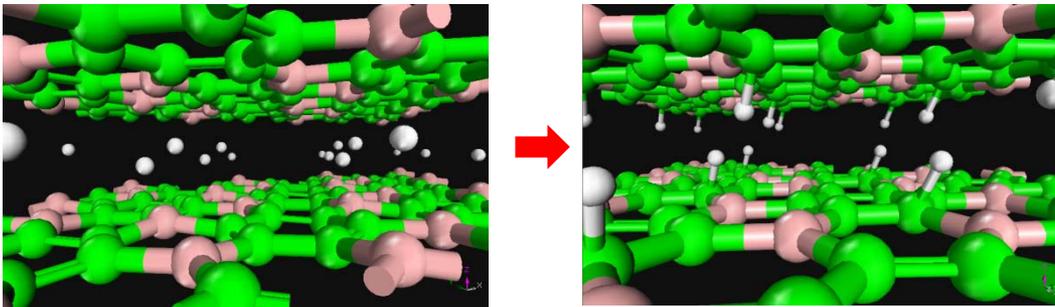
H₂ dissociation can be activated via orbital interaction between σ -orbital of H₂ (HOMO) and the empty p_z-orbital of B, leading to C-H bond formation

Technical Accomplishments – Understanding H₂ Dissociative Chemisorption in Bulk BC₃

H₂ diffusion into BC₃ pore: facile



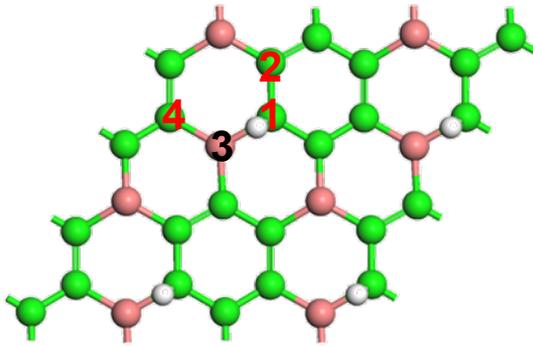
H₂ dissociation inside BC₃: facile



H₂ dissociative chemisorption in bulk BC₃ is energetically possible

Technical Accomplishments – Identification of Barriers for Migration of Chemisorbed Hydrogen on BC_3 Sheets

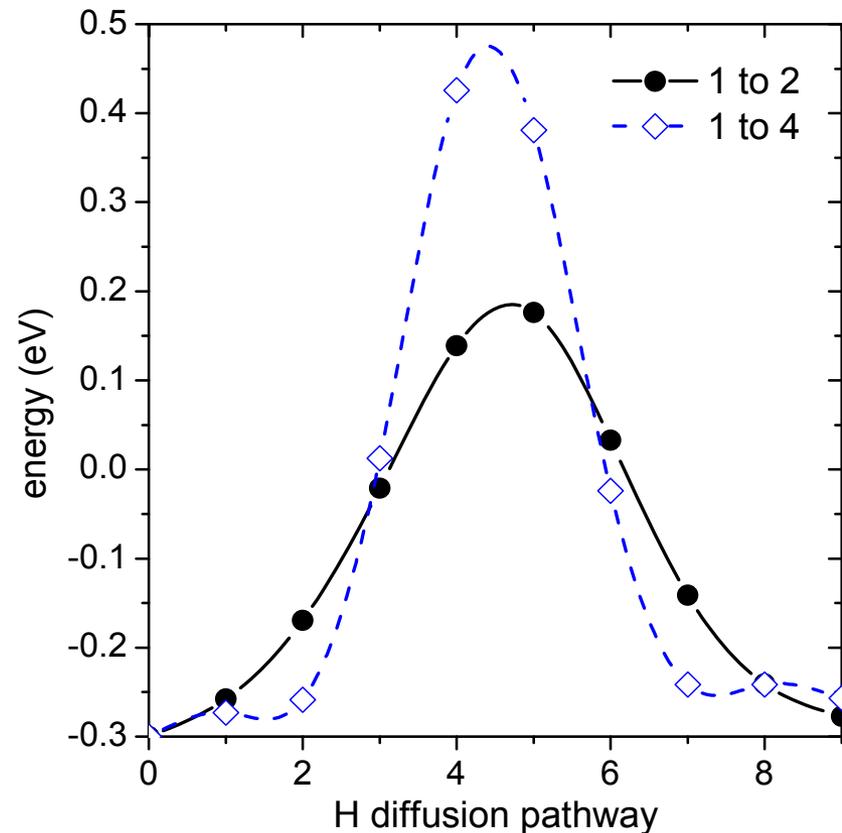
H diffusion inside BC_3



Barrier for 1 \rightarrow 2: ~ 0.47 eV

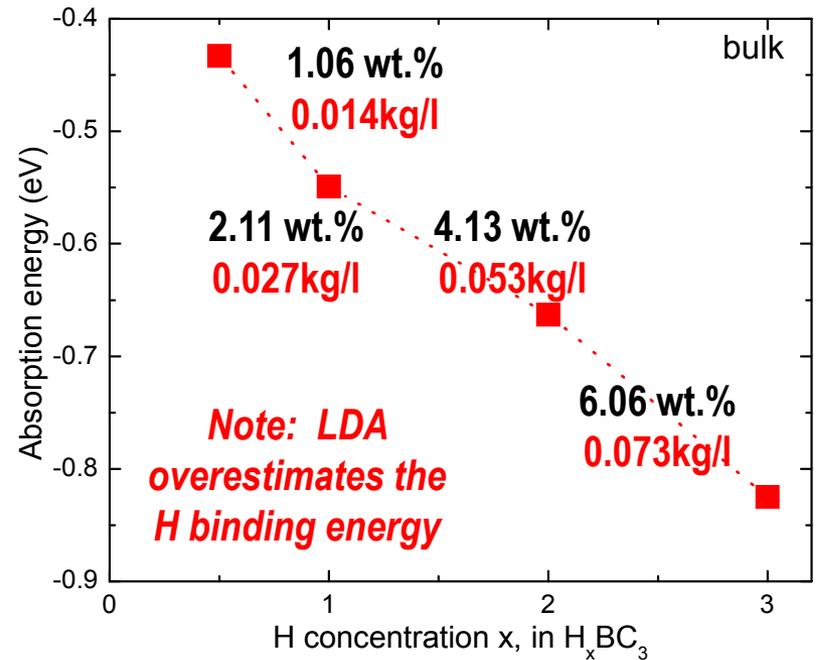
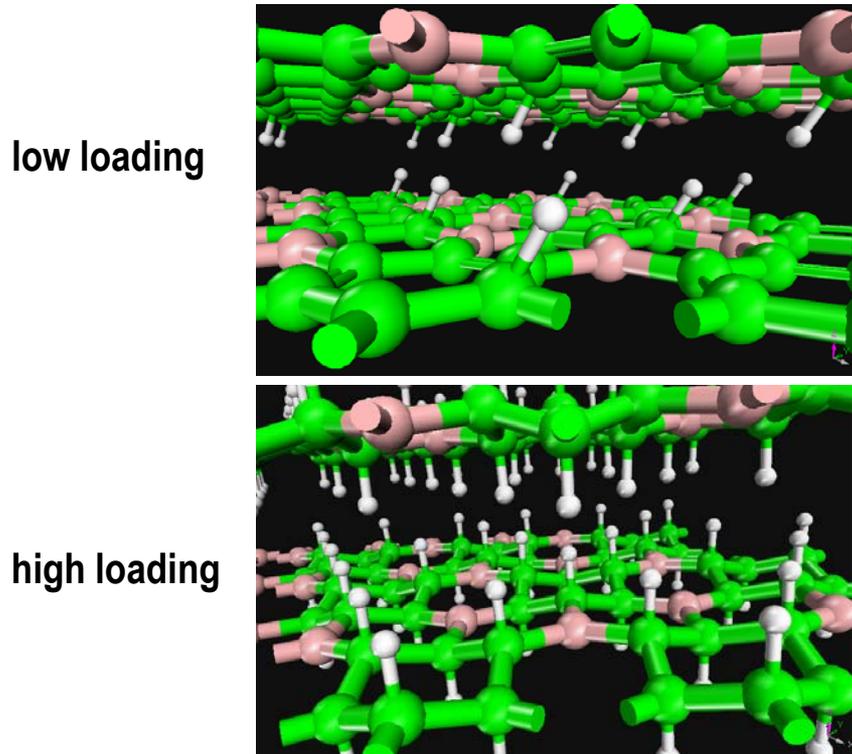
Barrier for 1 \rightarrow 4: ~ 0.78 eV

Barrier for 1 \rightarrow 3: ~ 1.30 eV



Long-range diffusion of chemisorbed H may be prevented by large barriers for diffusion steps that require $C \rightarrow B$ transfer of hydrogen

Technical Accomplishments – Calculation of H_2 Adsorption Energy in Bulk BC_3



H_2 dissociative chemisorption in bulk BC_3 is energetically possible, but chemisorbed H may be too stable at high loadings for reversibility

Collaborations

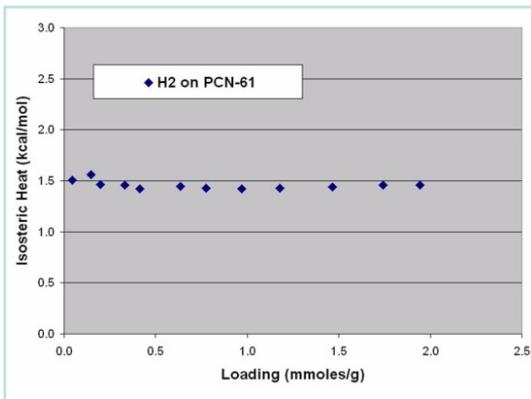
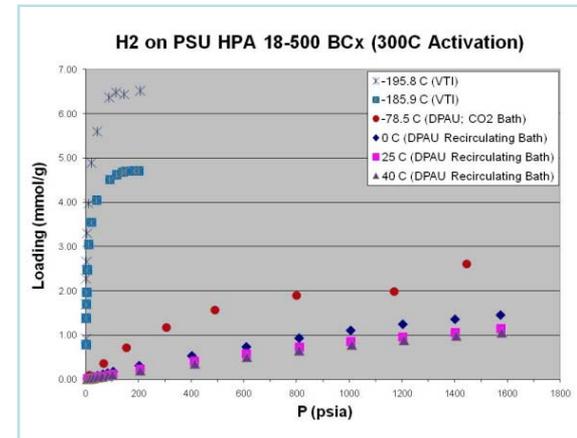
Pennsylvania State University

Chung Research Group:

Measurement of hydrogen isotherms and exchange of ideas on materials development

Foley Research Group:

Measurement of hydrogen spillover on Pt/C samples



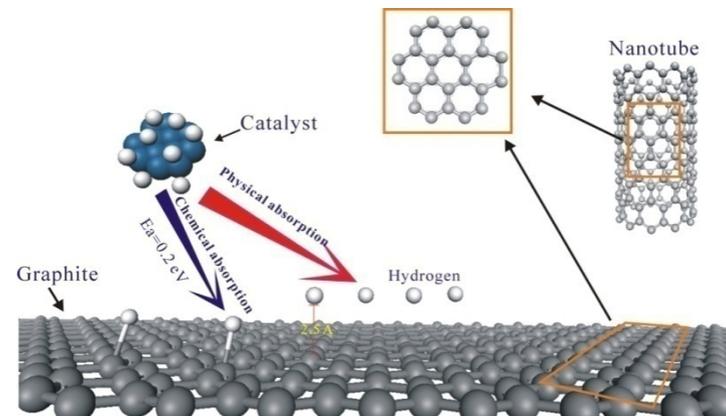
Texas A&M University

Measurement of hydrogen isotherms and isosteric heats (joint publication)

NREL, Rice University,

University of Michigan

Coordination of computational modeling of hydrogen spillover



Proposed Future Work

- Computational Modeling
 - Study incorporation of other heteroatoms in BC_3 to modify hydrogen chemisorption energies → promote reversibility of hydrogen adsorption
 - Understand the thresholds for hydrogen physisorption/chemisorption in BC_x materials
 - Predictive computational modeling of new BC_x materials
- Materials Development
 - Develop strategies for increasing surface area of BC_x materials (collaboration with M. Chung – Penn State University)
 - Develop a systematic model of B content and H_2 adsorption enthalpy using isosteric heat determinations and, potentially, calorimetry
- Adsorption Characterization
 - Explore utility of H_2 surface area determination for microporous adsorbents developed in the current project and HSCoE partner projects

Summary

- Fluoride materials were a good idea but we found the fundamental limits were far too low for practical H₂ storage materials
- A good alternative are boron-containing carbon – higher heats, possibility for high surface areas
- Use of modeling as a guide for synthetic targets appears to yield promising approaches