

# Discovery of Materials with a Practical Heat of H<sub>2</sub> Adsorption

Alan Cooper, Hansong Cheng, Wade Bailey,  
Xianwei Sha, Garret Lau, John Zielinski,  
Guido Pez

Air Products and Chemicals, Inc.

May 22, 2009

ST\_28\_Cooper

# 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)

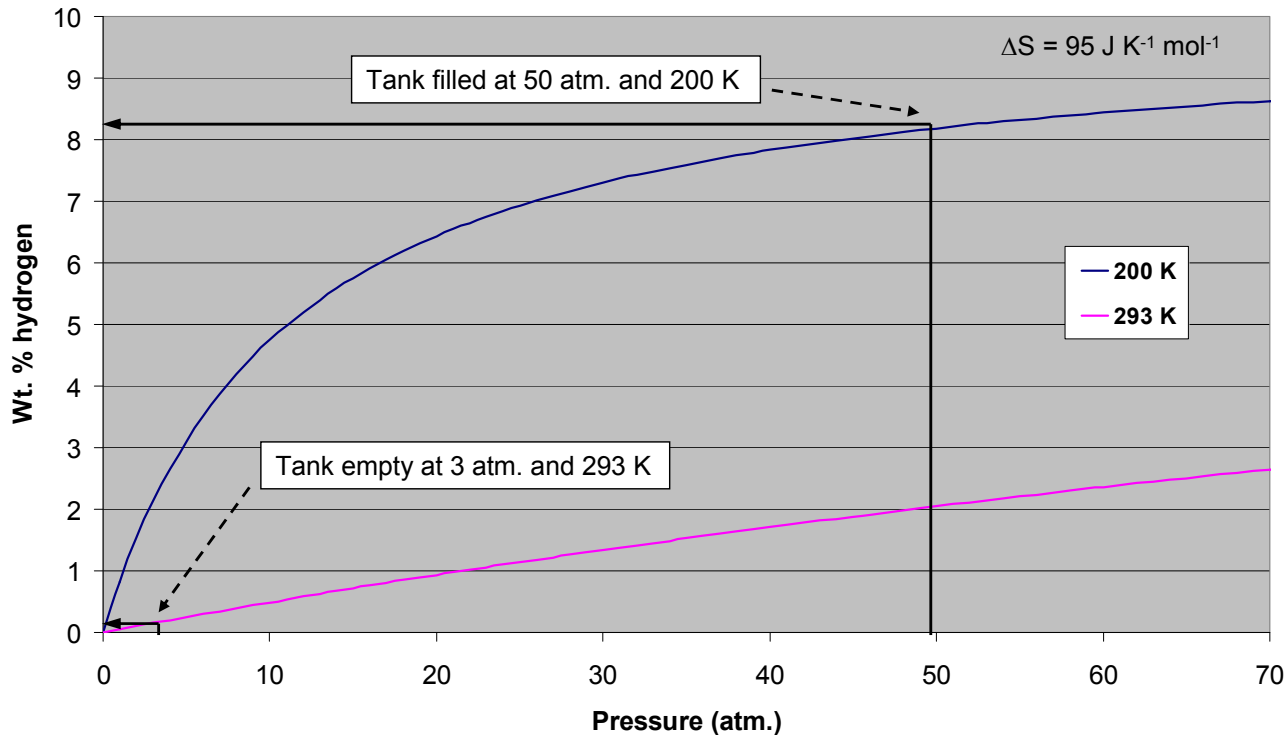
## Barriers

- 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 H<sub>2</sub> storage density and appropriate enthalpy of hydrogen adsorption for operation of hydrogen storage systems at practical engineering pressures and temperatures:
  - This task addresses H<sub>2</sub> 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 H<sub>2</sub> storage materials development by HSCoE partners:
  - This task addresses H<sub>2</sub> 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 H<sub>2</sub> storage measurements
  - Measurement of hydrogen isotherms for HSCoE partners (~25% of available instrument time)

# Relevance – Enhanced Physisorption



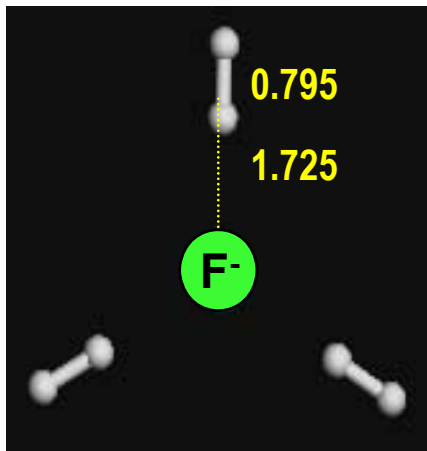
Simulated Langmuir isotherms at 200 and 293 K for an adsorbent with  $\Delta H = 15 \text{ kJ/mol}$  (assumptions: maximum capacity = 10 wt. %,  $\Delta S = 95 \text{ J K}^{-1} \text{ mol}^{-1}$ )

Physisorption of  $\text{H}_2$  using materials with a practical enthalpy can enable hydrogen storage systems that operate at moderate pressures and temperatures

# Approach – Technical Motivation

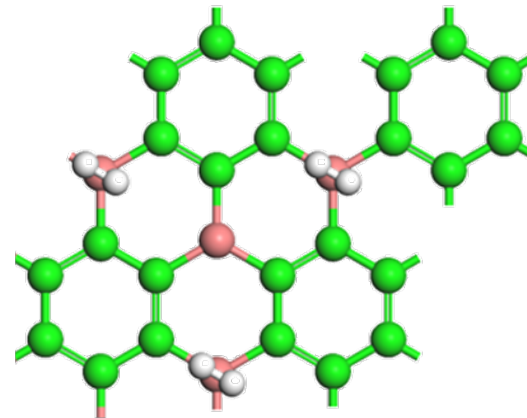
- How can we enable and execute discovery of materials with enhanced enthalpy relative to “conventional” hydrogen storage materials (eg. activated carbon)?
  - Interaction of hydrogen with either electron-deficient species (electrophiles, Lewis acids) or very strong electron donors (Lewis bases)

Interaction of H<sub>2</sub> with a fluoride anion



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

Adsorption of H<sub>2</sub> on boron atoms of BC<sub>3</sub>



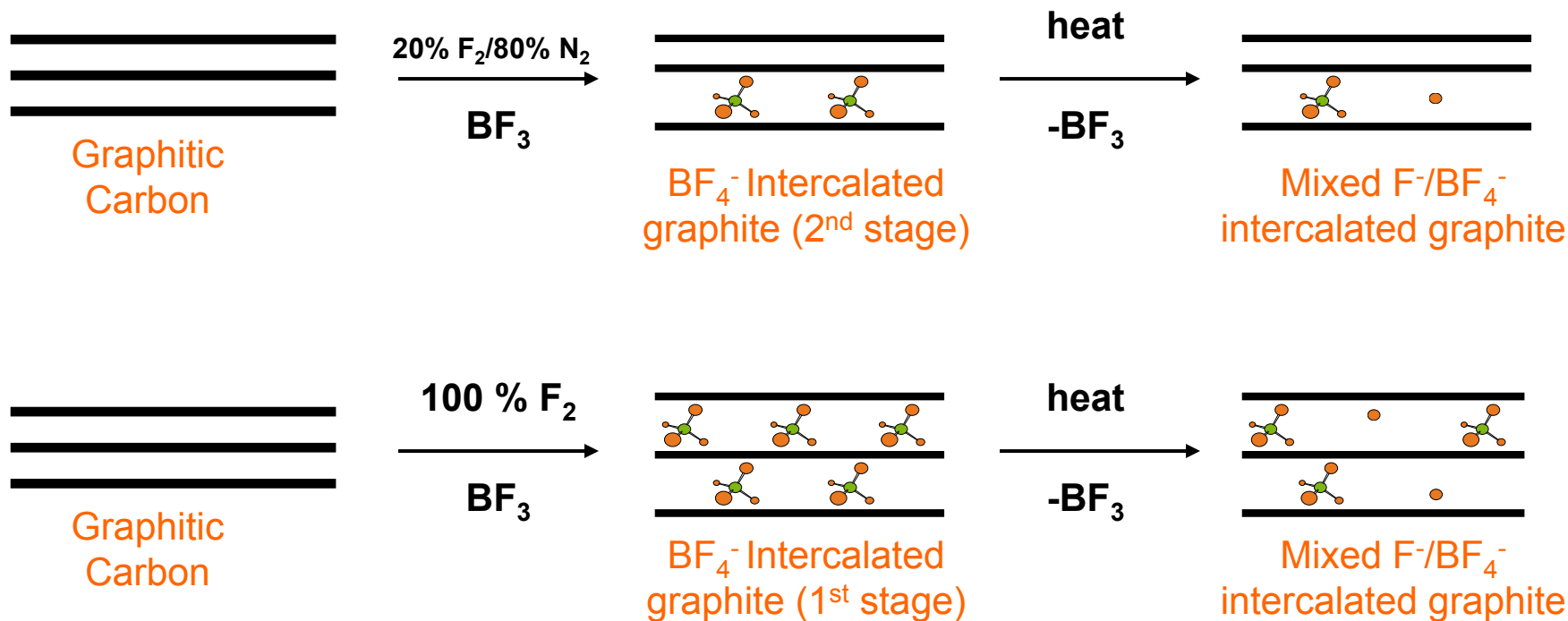
# Approach – Discovery of New H<sub>2</sub> Storage Materials

- Translate predictive computational modeling to development and testing of new H<sub>2</sub> storage materials
  - Novel materials development based upon theoretical predictions of high H<sub>2</sub> 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 H<sub>2</sub> isotherms
  - Surface area determination using H<sub>2</sub> condensation as a more informative alternative to conventional N<sub>2</sub> 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

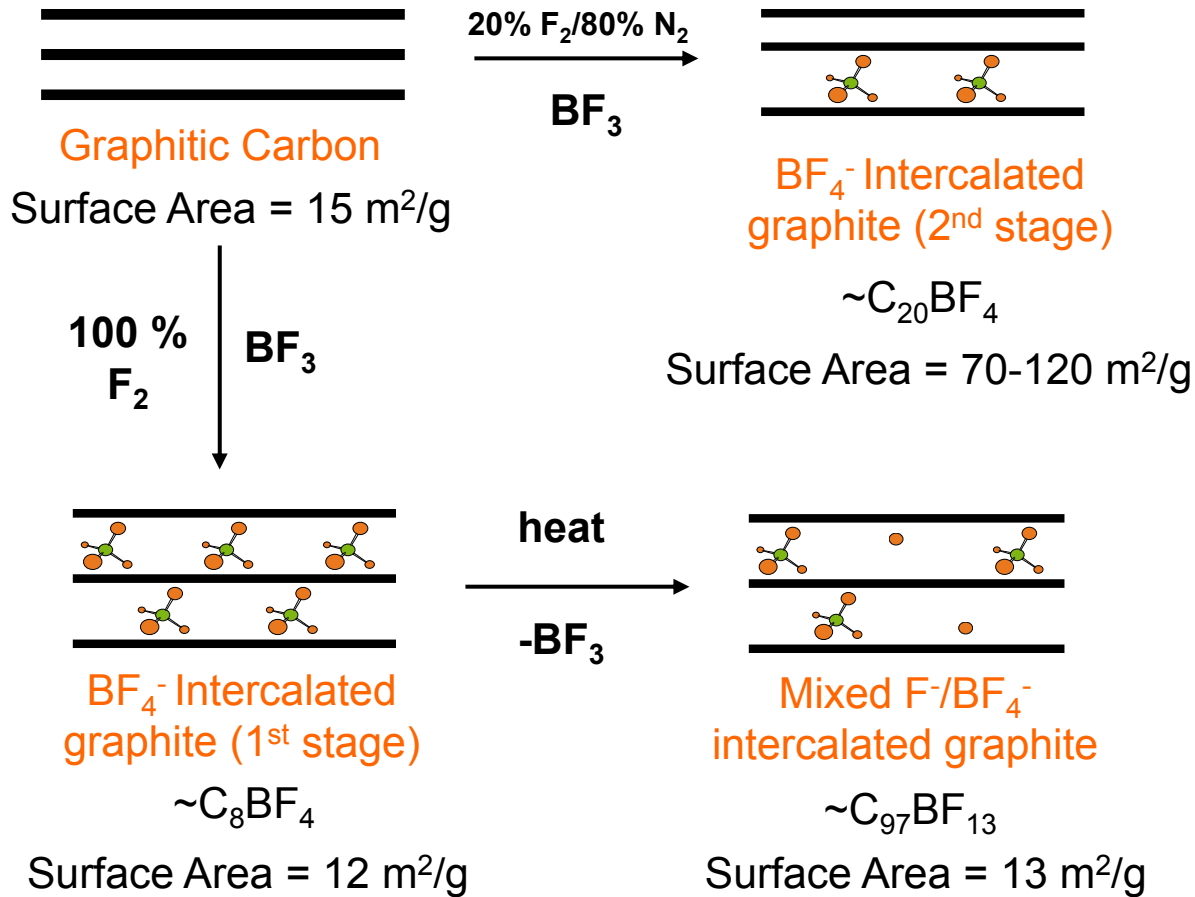
# Technical Accomplishments – Synthesis of F<sup>-</sup>/BF<sub>4</sub><sup>-</sup> Graphite Intercalation Compounds (GIC)



Our upgraded experimental procedure has facilitated the use of pure F<sub>2</sub> which allowed the synthesis of 1<sup>st</sup> stage BF<sub>4</sub><sup>-</sup> intercalated graphite

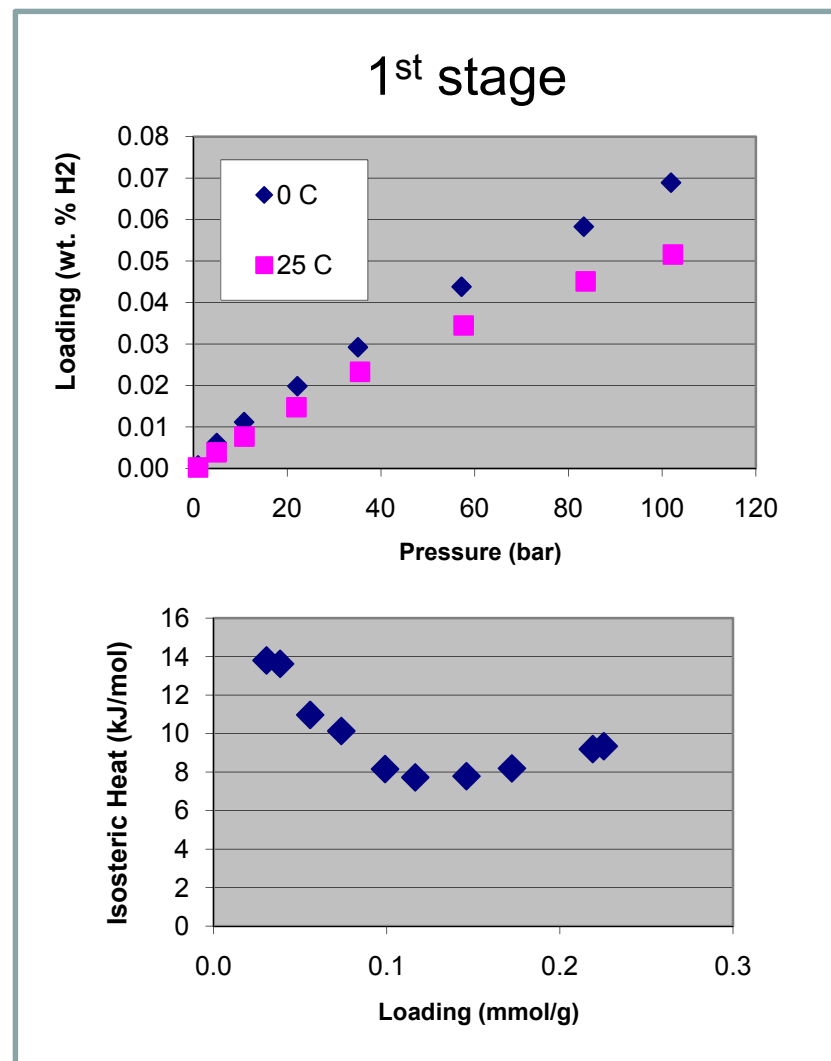
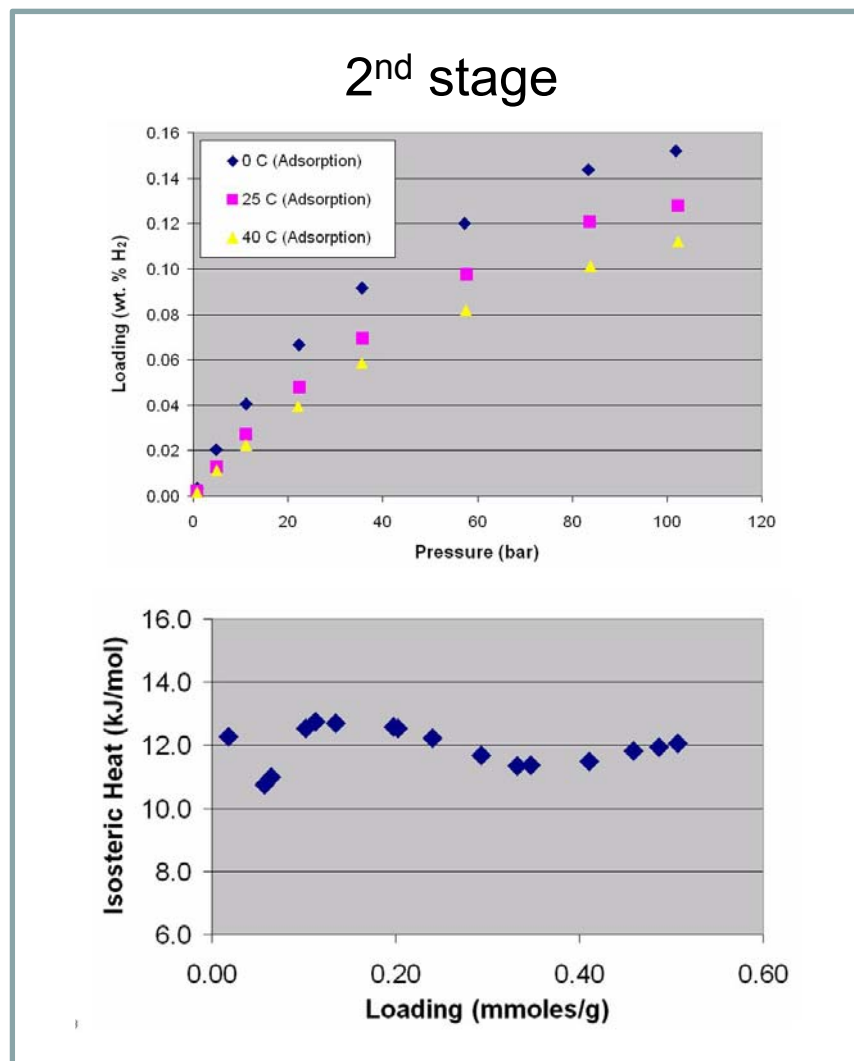


# Technical Accomplishments – Creation of Microporosity by Anion Intercalation



1<sup>st</sup> stage GIC shows no improvement in surface area

# Technical Accomplishments – Comparison of H<sub>2</sub> isotherms on 1<sup>st</sup> and 2<sup>nd</sup> Stage Compounds



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

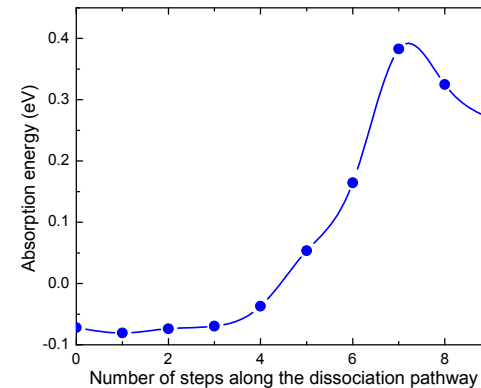
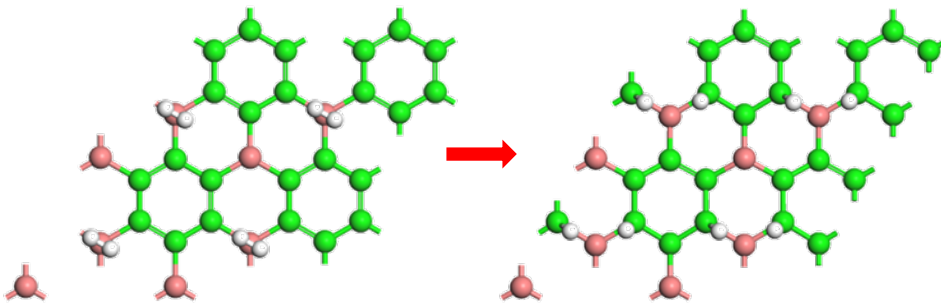
Elemental Analysis indicates low levels of intercalation and covalent C-F bond formation (fluorination)

Isosteric heat calculations indicate little enhancement of H<sub>2</sub> adsorption enthalpy relative to host materials

# Background - Hydrogen Spillover in BC<sub>3</sub>

Published LDA calculations indicate that H<sub>2</sub> undergoes spontaneous dissociation in bulk BC<sub>3</sub>  
Zhang and Alavi (J. Chem. Phys. 2007, 127, 214704)

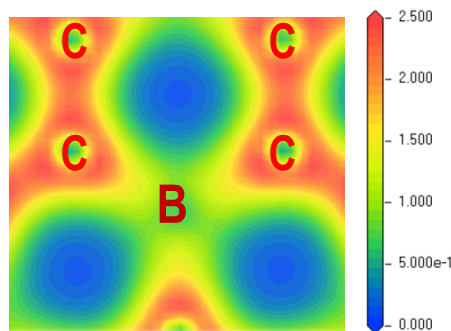
H<sub>2</sub> dissociative chemisorption on a BC<sub>3</sub> sheet:



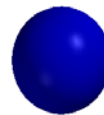
moderate  
barrier

endothermic  
reaction

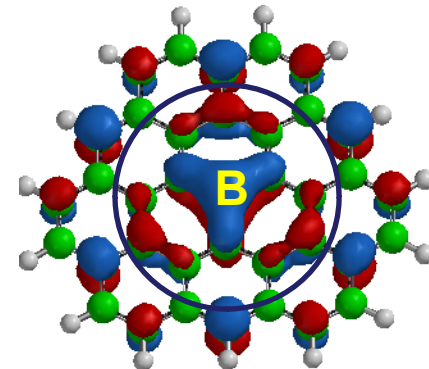
Electron density:



Orbital interaction:



H<sub>2</sub> HOMO ( $\sigma$ -orbital)

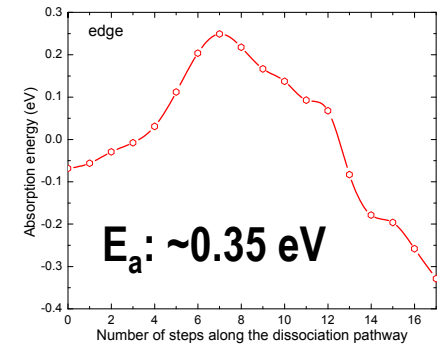
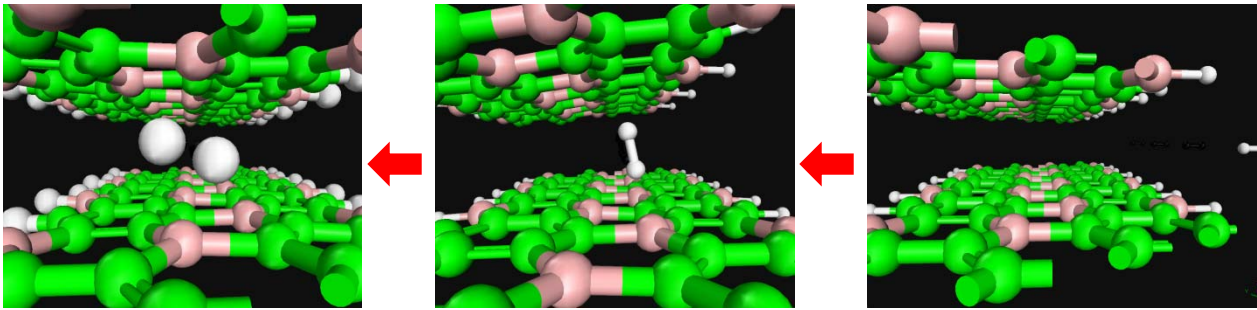


LUMO

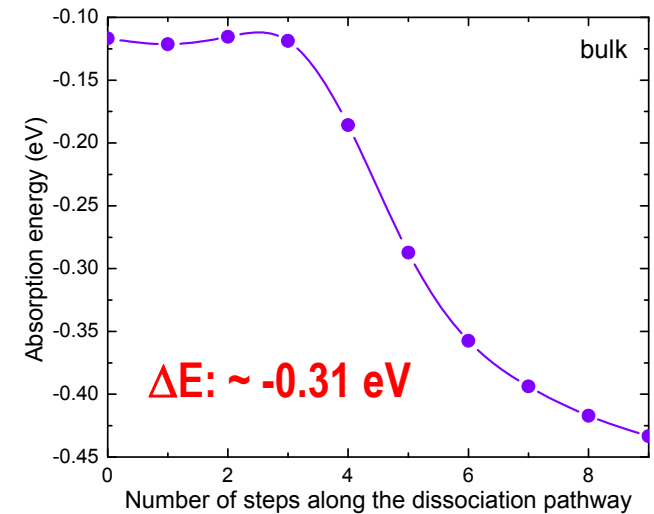
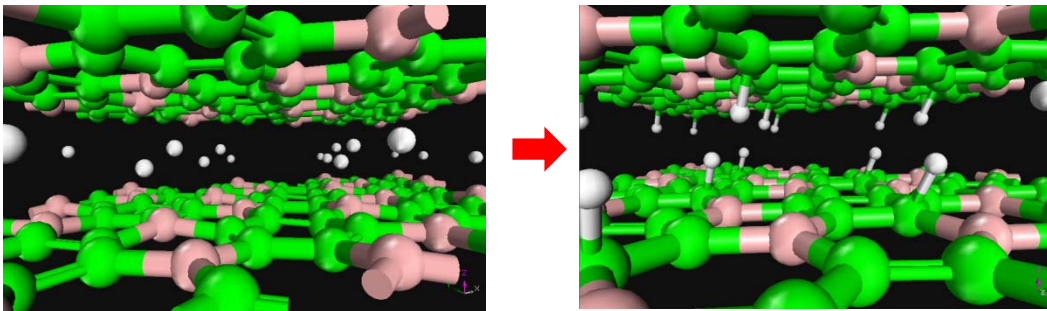
H<sub>2</sub> dissociation can be activated via orbital interaction between  $\sigma$ -orbital of H<sub>2</sub> (HOMO) and the empty p<sub>z</sub>-orbital of B, leading to C-H bond formation

# Technical Accomplishments – Understanding H<sub>2</sub> Dissociative Chemisorption in Bulk BC<sub>3</sub>

H<sub>2</sub> diffusion into BC<sub>3</sub> pore: facile



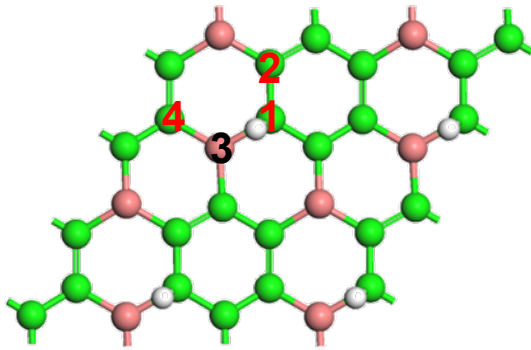
H<sub>2</sub> dissociation inside BC<sub>3</sub>: facile



H<sub>2</sub> dissociative chemisorption in bulk BC<sub>3</sub> is energetically possible

# Technical Accomplishments – Identification of Barriers for Migration of Chemisorbed Hydrogen on BC<sub>3</sub> Sheets

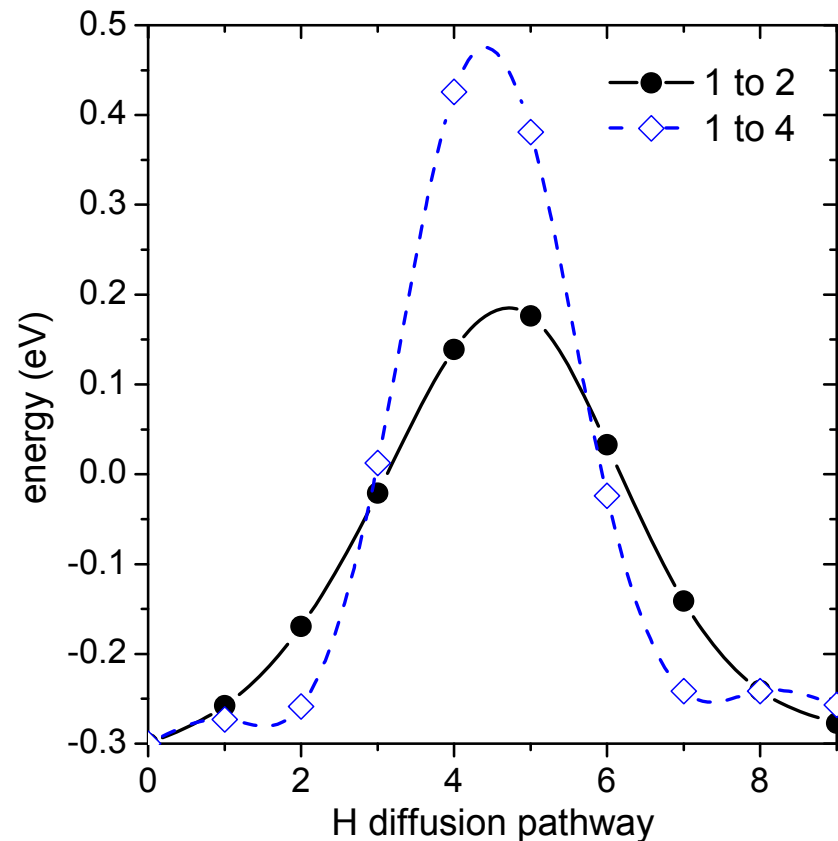
## H diffusion inside BC<sub>3</sub>



**Barrier for 1 → 2: ~ 0.47 eV**

**Barrier for 1 → 4: ~ 0.78 eV**

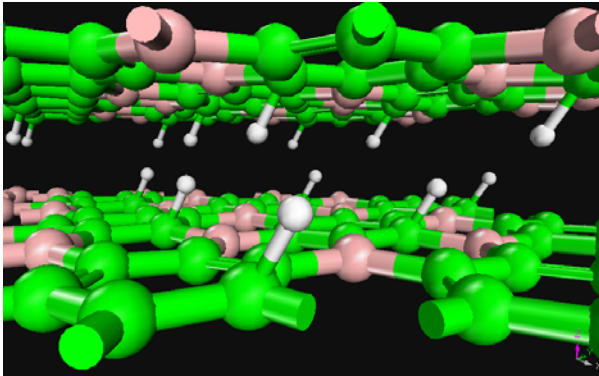
**Barrier for 1 → 3: ~ 1.30 eV**



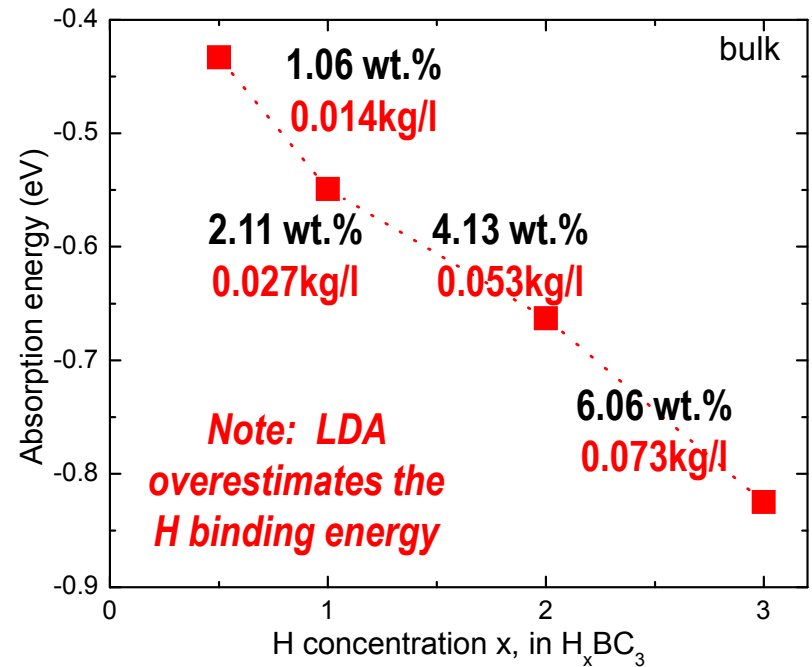
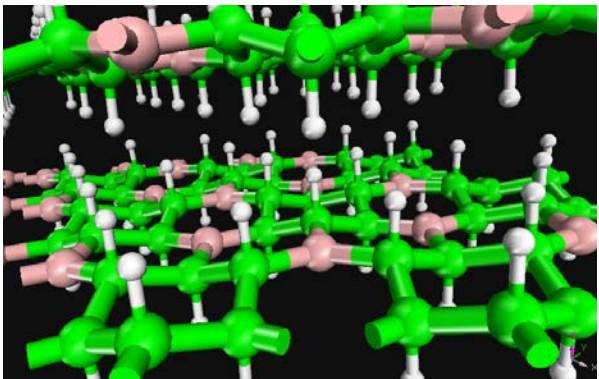
Long-range diffusion of chemisorbed H may be prevented by large barriers for diffusion steps that require C → B transfer of hydrogen

# Technical Accomplishments – Calculation of H<sub>2</sub> Adsorption Energy in Bulk BC<sub>3</sub>

low loading



high loading



H<sub>2</sub> dissociative chemisorption in bulk BC<sub>3</sub> is energetically possible, but chemisorbed H may be too stable at high loadings for reversibility



# Collaborations

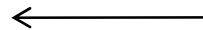
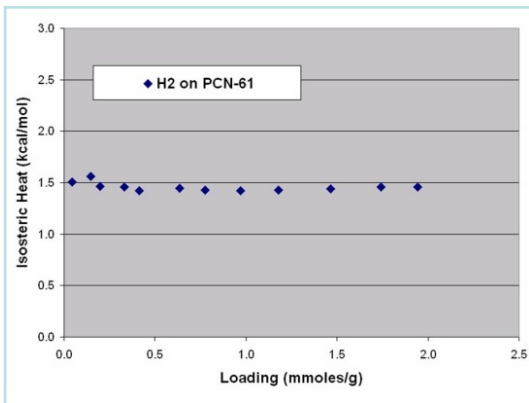
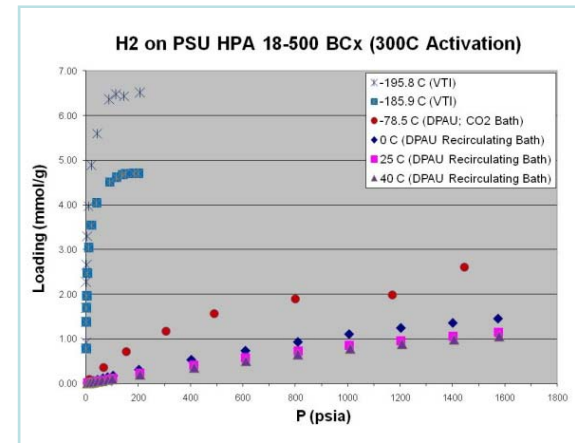
Pennsylvania State University

**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



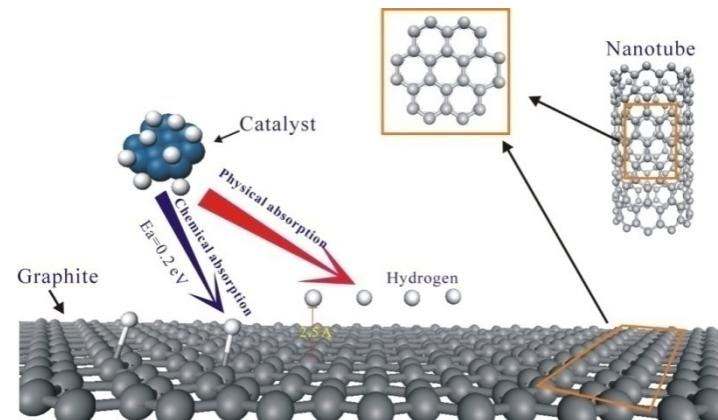
Texas A&M University

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 H<sub>2</sub> 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