Discovery of Materials With a Practical Heat of H_2 Adsorption

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ST082

Overview

Timeline

- Project start date: 3/1/05
- Project end date: 8/28/10
- ~97% complete

Budget

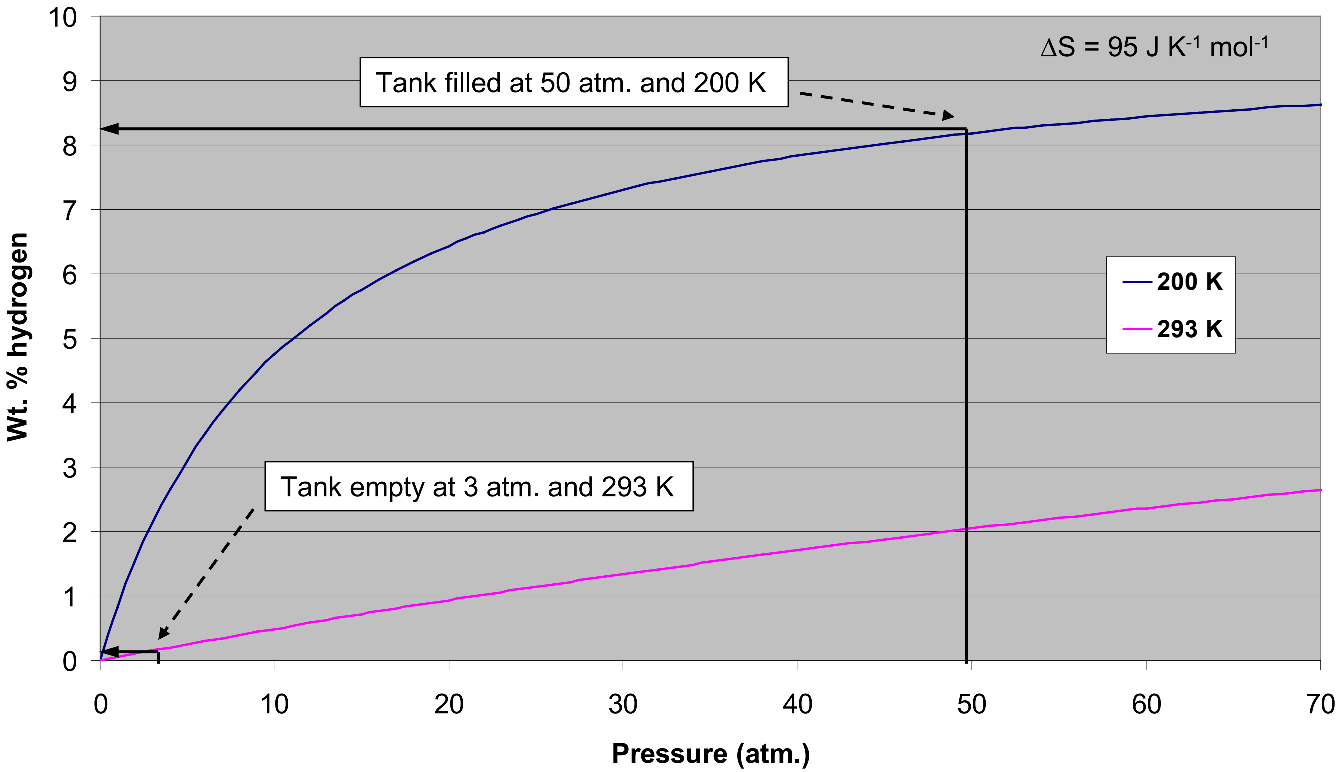
- Total project $3,689,645
  - DOE share $2,951,716 (80%)
- FY09 funding $750,000
- FY10 funding $100,000

Barriers

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

Partners

Relevance: Benefits of Enhanced Physisorption on H_2 Storage System Design



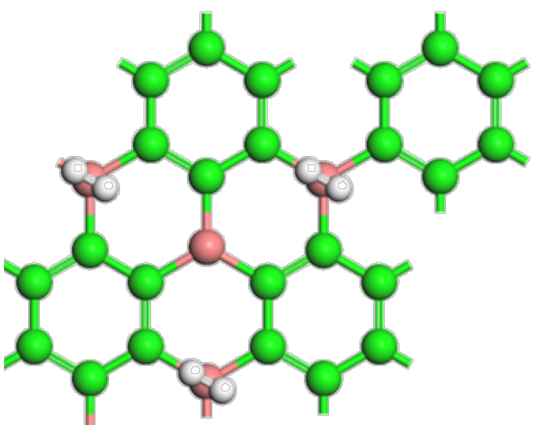
Simulated Langmuir isotherms at 200 and 293 K for an adsorbent with ΔH = 15 kJ/mol (assumptions: max. capacity = 10 wt. %, $\Delta S = 95\ J\ K^{-1}\ mol^{-1}$)

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

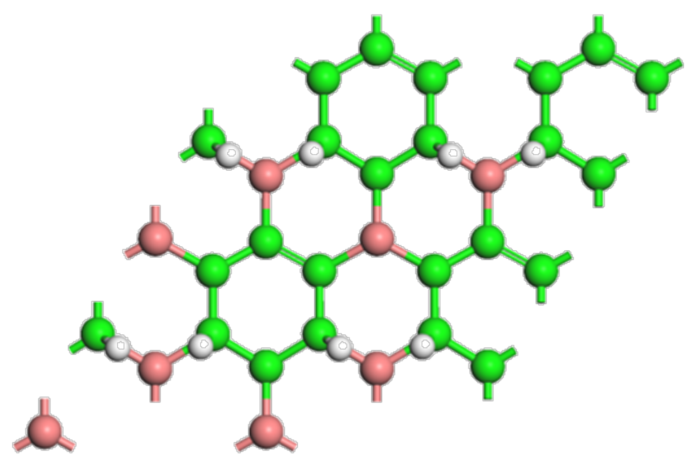
Approach: Technical Motivation

- 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 electron-deficient species (electrophiles, Lewis acids) and potential for additional hydrogen storage density by reversible hydrogen spillover mediated by the presence of boron in the spillover receptor

Adsorption of H_2 on BC_3



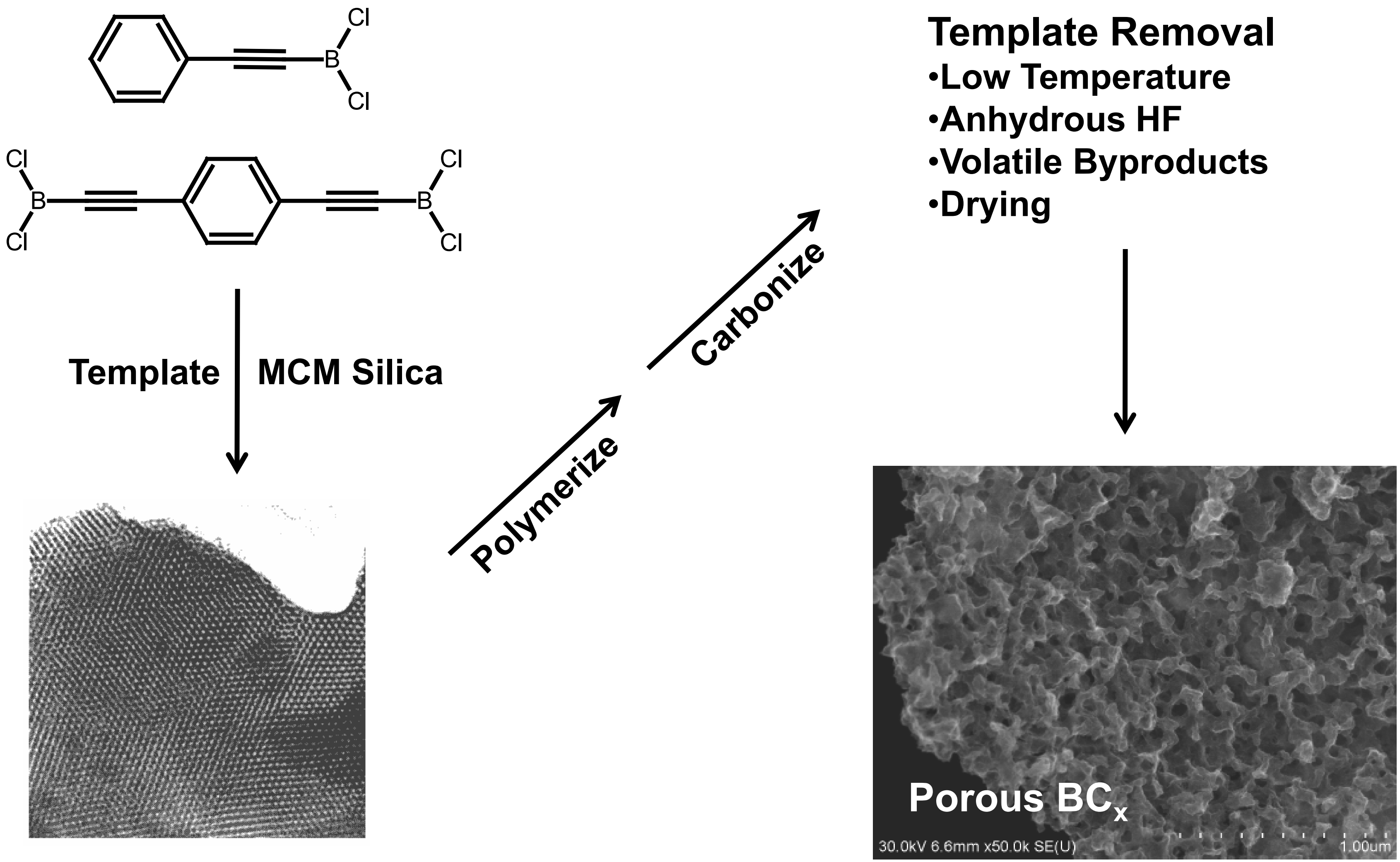
Chemisorption of hydrogen on BC_3



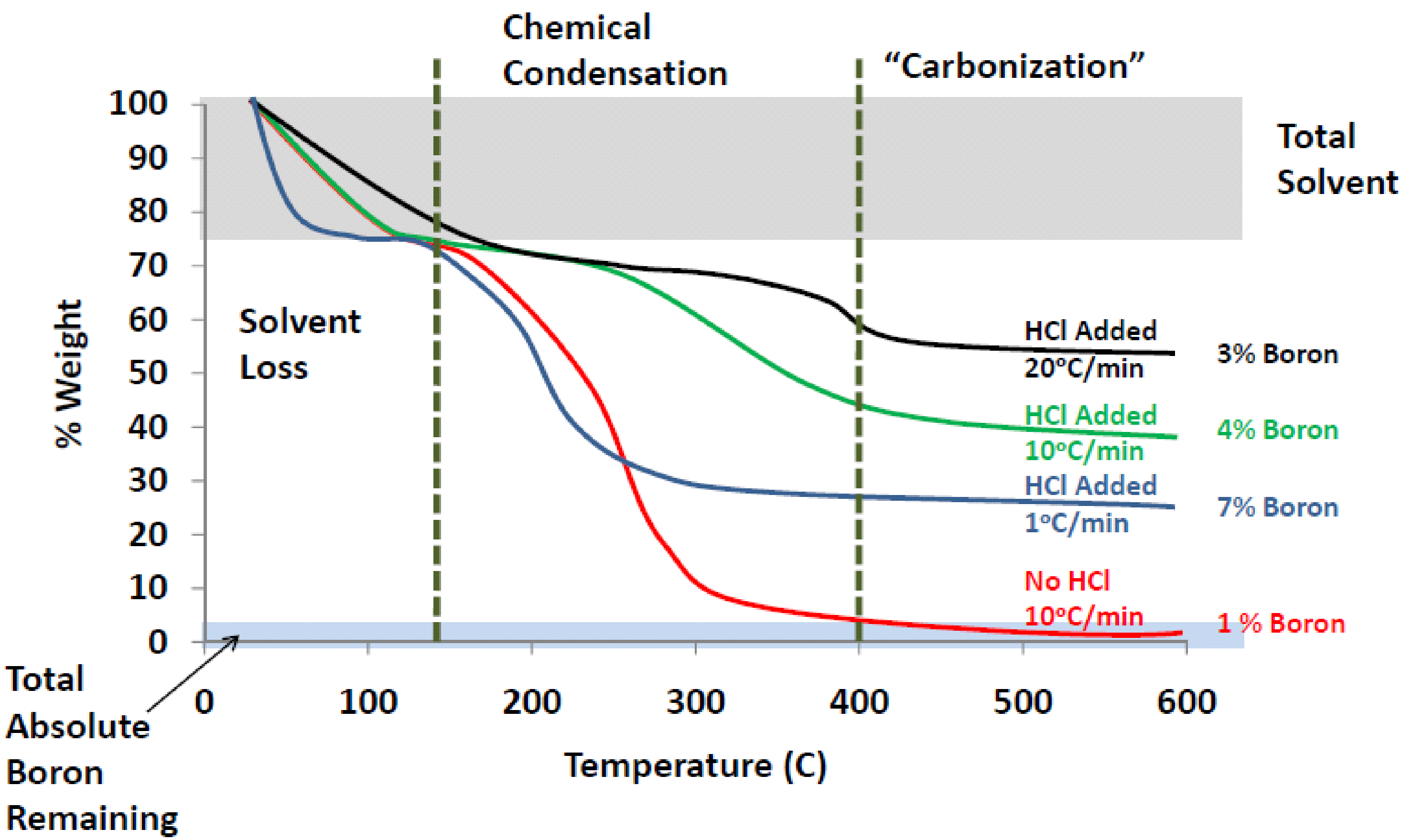
Approach: Methods for Discovery of New H_2 Storage Materials

- Translate predictive computational modeling to development and testing of new H_2 storage materials
  - Novel materials development based upon theoretical predictions of high H_2 adsorption enthalpy and/or reversible chemisorption of hydrogen
  - Materials synthesis (novel approaches to boron-containing carbon materials with high surface area)
- General quantitative computational models for new materials discovery
  - Through collaborative efforts within the HSCoE, realize a more practical overlap between computational and experimental work (e.g., modeling mechanism of hydrogen spillover)

Technical Accomplishments: Template-structured BC_x Sorbents for H_2

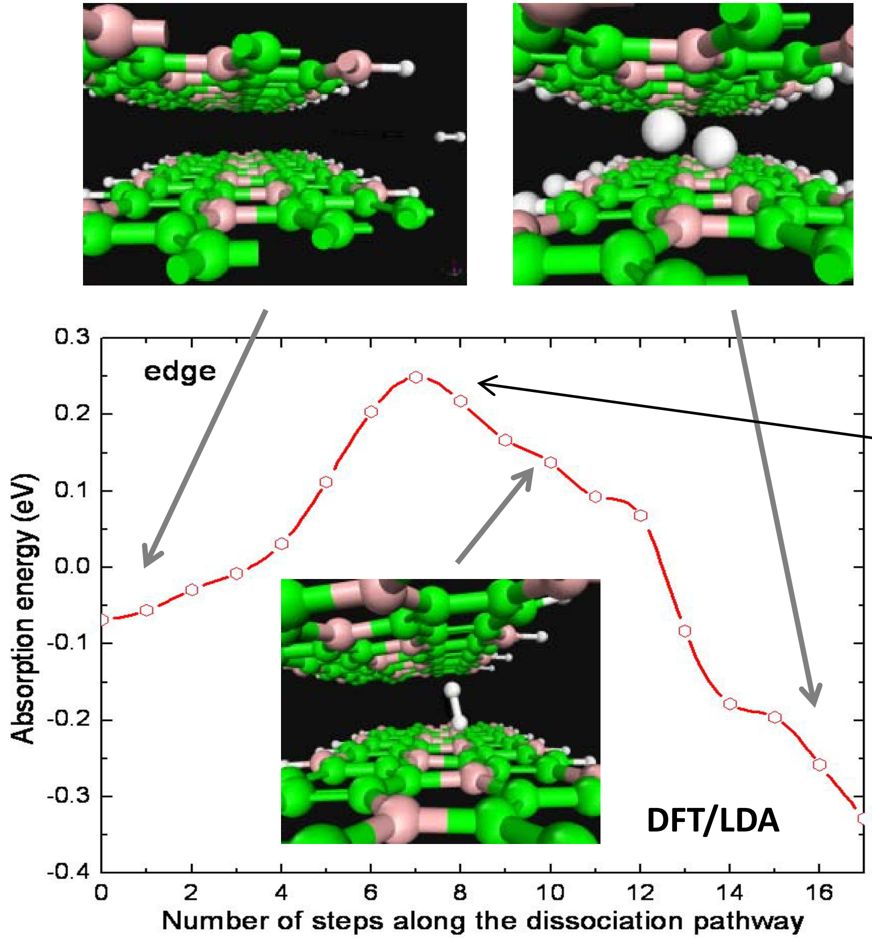


Technical Accomplishments: Understanding of Carbonization Conditions to Enhance Boron Content of BC_x Sorbents



Treatment with acid helps with boron retention by promoting polymerization prior to carbonization

Technical Accomplishments: Calculated Energies for H_2 Diffusion and Chemisorption in Bulk BC_3

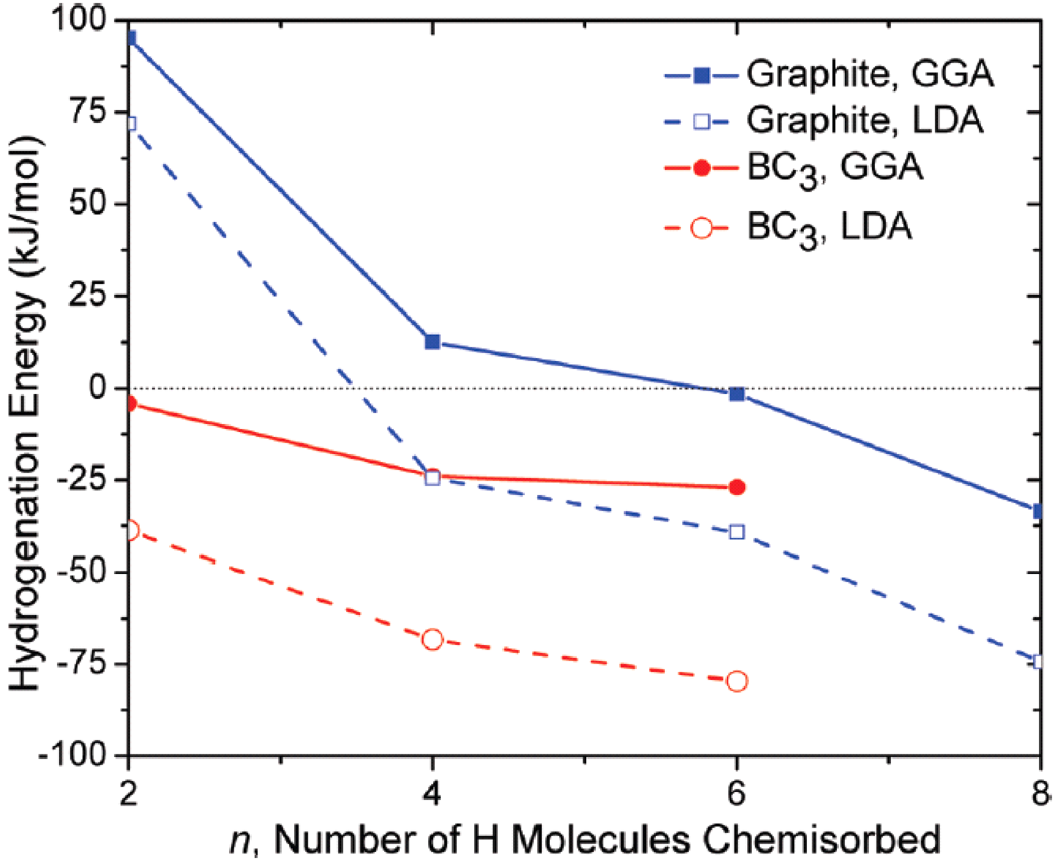


There is a modest barrier of ca. 0.3 eV for the penetration of hydrogen into bulk BC_3

The DFT/LDA method predicts that the chemisorption of hydrogen is exothermic

This reactivity with hydrogen is unique to BC_3. The same process will not occur with graphite in the absence of a catalyst to dissociate hydrogen.

Technical Accomplishments: Calculated Energies for H_2 Diffusion and Chemisorption in Bulk BC_3

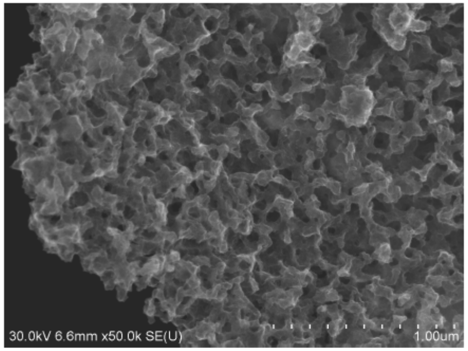


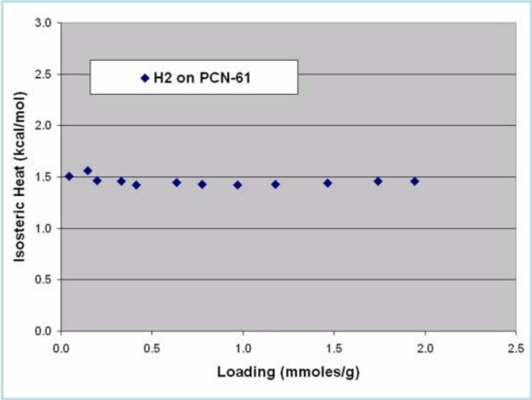
Hydrogenation energy in bulk graphite and BC_3 as a function of the number of H_2 molecules chemisorbed in the unit cell. The results using both LDA and GGA approximations are presented (There are a total of 8 boron/carbon atoms in the unit cells).

The more accurate GGA method shows that hydrogenation of BC_3 is only modestly exothermic → This suggests that the C-H bonds are relatively weak

Collaborations: Examples

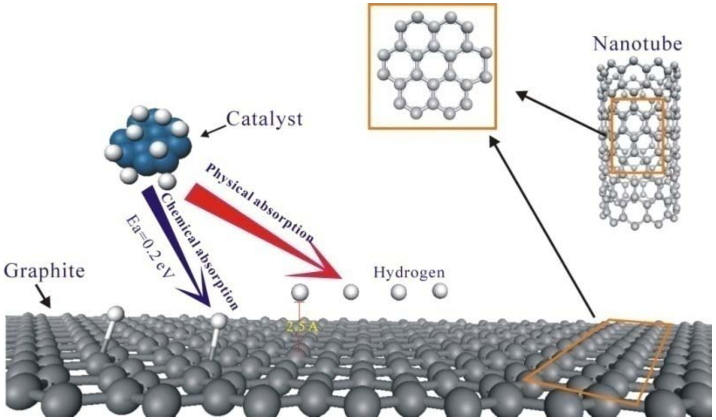
Pennsylvania State University
Measurement of hydrogen isotherms and exchange of ideas on materials development



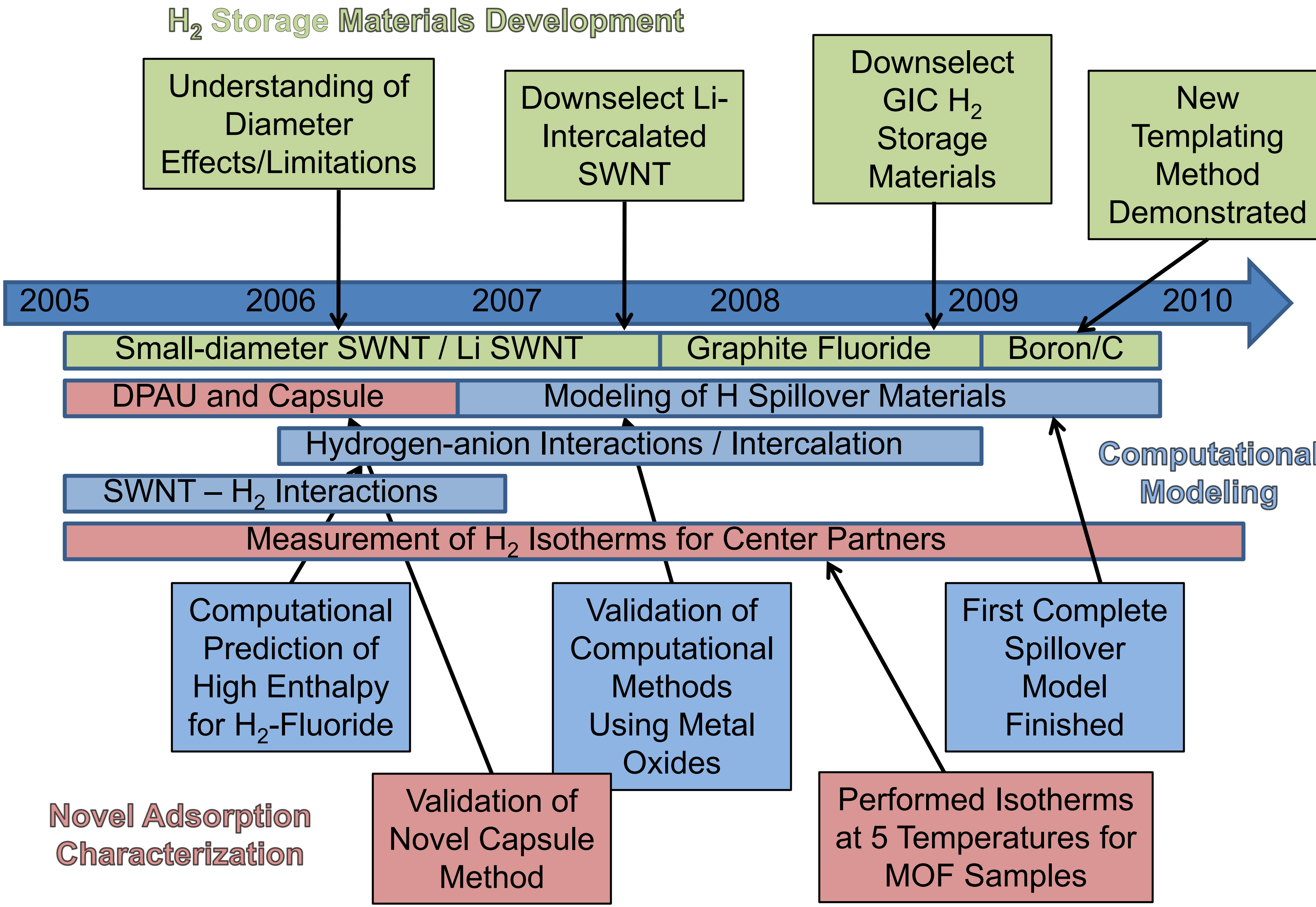


Texas A&M University
Measurement of hydrogen isotherms and isosteric heats for MOF samples

NREL, Rice University, University of Michigan
Coordination of computational modeling of hydrogen spillover



Overview: Work Performed Under This Project



Overview: Project Successes

- Produced a comprehensive experimental and theoretical understanding of hydrogen adsorption on singlewalled carbon nanotubes (SWNT)
  - Increase of hydrogen adsorption enthalpy for small-diameter SWNT
  - Mechanistic insights/role of pore selectivity
  - Lithium intercalation to increase hydrogen adsorption enthalpy
  - 3 publications and 1 publication in progress
- Demonstration of high-enthalpy hydrogen adsorption on anion-intercalated materials and boron-containing carbons
  - Graphite fluoride and templated boron-containing carbons
  - 2 publications and 2 publications in progress
- Development of robust and sensitive methods for measuring hydrogen adsorption [e.g. Differential Pressure Adsorption Unit (DPAU)]
  - Allowed accurate isotherm measurements on small samples at near-ambient temps. (<100 mg sample sizes)
  - Novel approaches were developed and published (eg. "capsule" method)
  - 2 publications
- Provided mechanistic details and guidance for experimental spillover studies
  - First computational model of the entire spillover process (H2 dissociation → Spillover to material → Migration into/onto bulk material)
  - Metal oxides (as a test of the method) and carbon-based materials
  - 7 publications