DOE Hydrogen Program

Enabling Discovery of Materials with a Practical Heat of H_2 Adsorption

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Overview

Timeline

- Project start date FY05
- Project end date FY10
- ~60% complete

Budget

- Total project $3,948,220
  - DOE share $3,158,575 (80%)
- FY07 funding $575,000
- FY08 funding $700,000

Barriers

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

Partners

- Current collaborations: Penn State, University of North Carolina, NIST (sample exchanges, sample characterization)
- Anticipated/other interactions: Rice University, NREL, ORNL, Univ. of Michigan (coordination of computational modeling efforts)

Objectives

- Development and testing of new materials with high H_2 storage density and appropriate enthalpy of hydrogen adsorption
  - We have leveraged existing materials science and chemistry capabilities in carbon materials and fluorine chemistry to generate new hydrogen storage materials for testing.
- Development of enabling technologies for H_2 storage materials development
  - We have used our accurate, predictive computational methodologies for new materials discovery and mechanistic understanding of hydrogen spillover.
  - We have continued our development of unique characterization tools for accurate H_2 storage measurements and used these to measure our new storage materials and partner samples.
- Our goal: reversible adsorption of hydrogen at near-ambient temperatures at densities that will enable meeting the 2010 DOE system-level targets for hydrogen storage

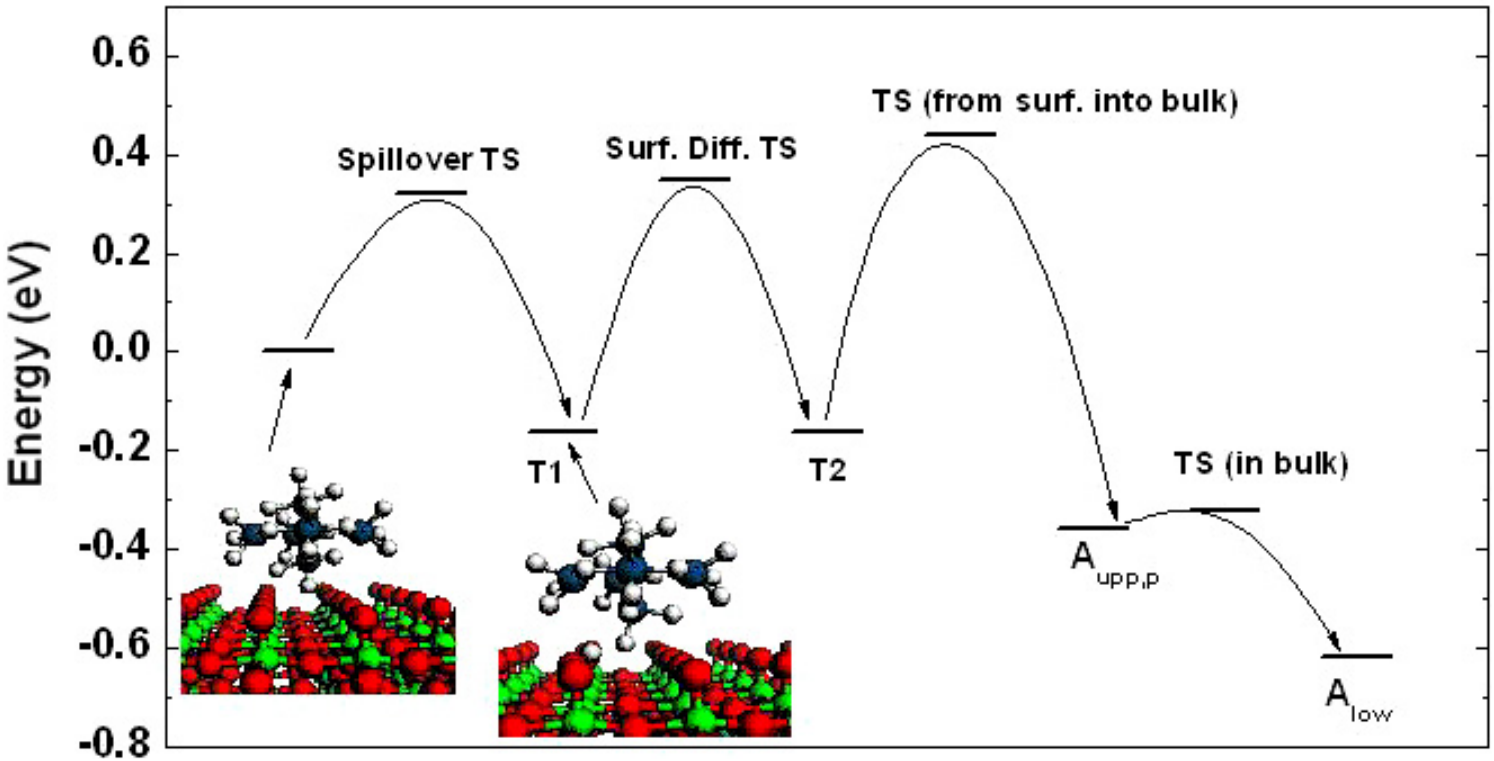
Milestones

	Milestone
4QFY08	Find optimal BF_4^-/F^- ratio for maximum H_2 uptake and/or heat of adsorption in intercalated graphite
1QFY09	Study BF_4^-/F^- intercalation of N-doped carbon with high N levels (nominal C_5N composition); obtain hydrogen isotherm data on these materials
3QFY08	Perform *ab initio* MD simulations and minimum energy path calculations on BC_3-intercalated compounds

Approach: How can we enable and execute discovery of materials with a higher heat of H_2 adsorption?

- 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 storage density and/or enthalpy
  - Materials synthesis (fluorine chemistry, novel carbon-based materials)
- General quantitative computational models for new materials discovery
  - Realize a more practical overlap between computational and experimental work (e.g., modeling mechanism of hydrogen spillover)
  - Highly collaborative within HS CoE
- Accurate measurement techniques
  - Correction for helium adsorption effects on H_2 isotherms

Accomplishments: Completed Computational Model of Hydrogen Spillover Process in MoO_3



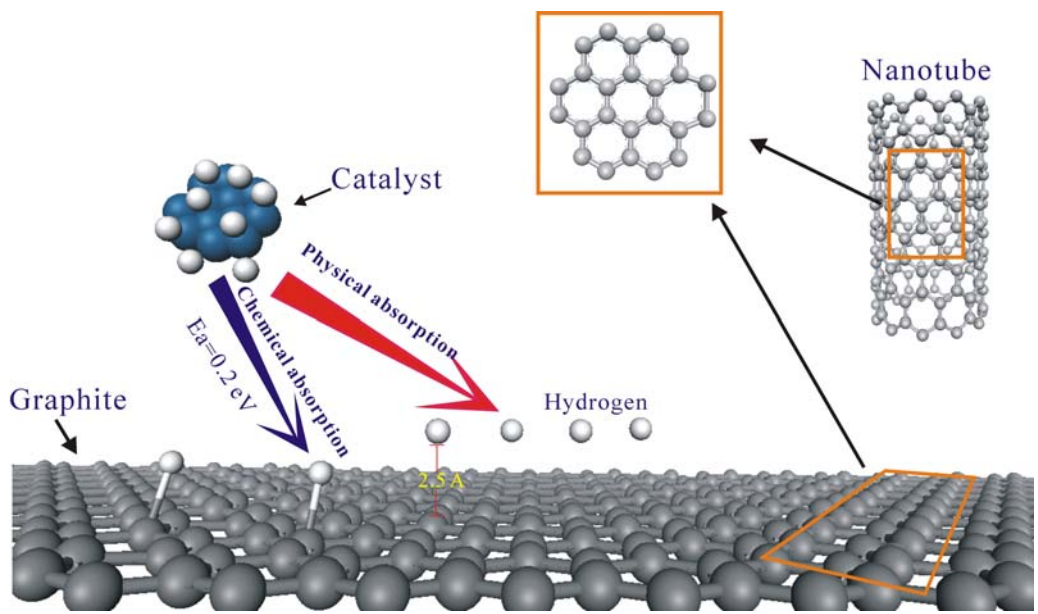
- Hydrogen spillover in MoO_3 is facilitated by the extensive H-bonding network → this understanding could benefit the development of carbon-based spillover materials

Hydrogen Spillover Mechanism – Graphitic materials

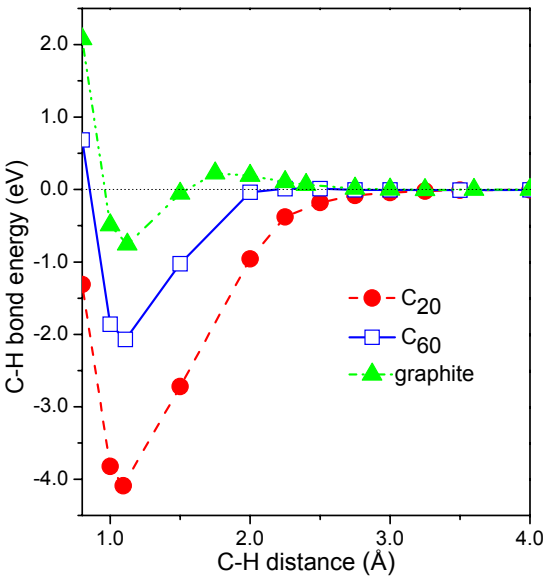
- H migration from Pt to substrate: facile (<0.5 eV/H)
- H diffusion via chemisorption: difficult (~0.9 eV/H)
- H diffusion via physisorption: facile (<0.02 eV/H)
- Physisorbed H atoms will either recombine into H_2 or form C-H bonds

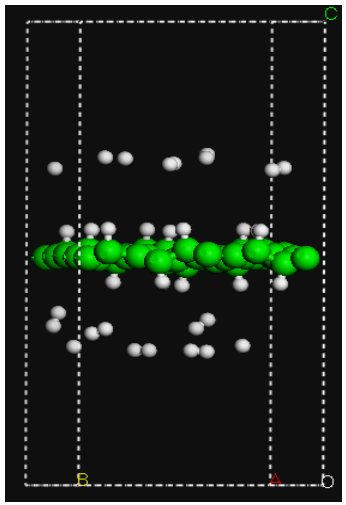
J.Phys. Chem. C 111, 18995 (2007); 112, 1755 (2008).

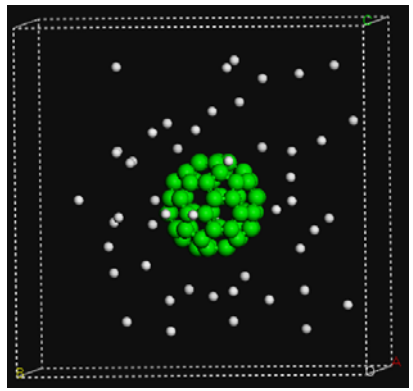
"On the dynamic behavior of physisorbed H atoms on graphitic carbon materials," submitted.

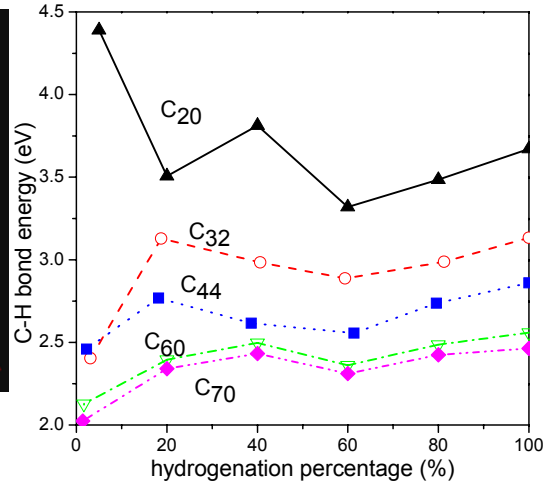


Predictive Model Developed for H Spillover Dynamics on Carbon Materials



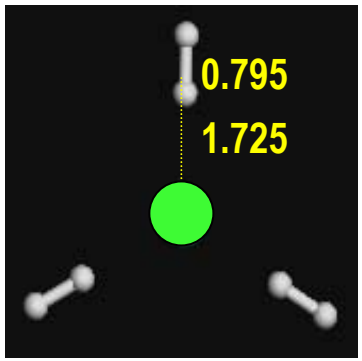






- Physisorption of H atoms is only metastable. H atoms will either further hydrogenate the substrates or recombine to form H_2.
- Hydrogen storage via spillover is curvature dependent (properly curved carbons, e.g. large diameter SWNT, can enhance spillover efficiency) → guidance to experimental efforts in CoE
- H desorption from small fullerenes or nanotubes will be very difficult.

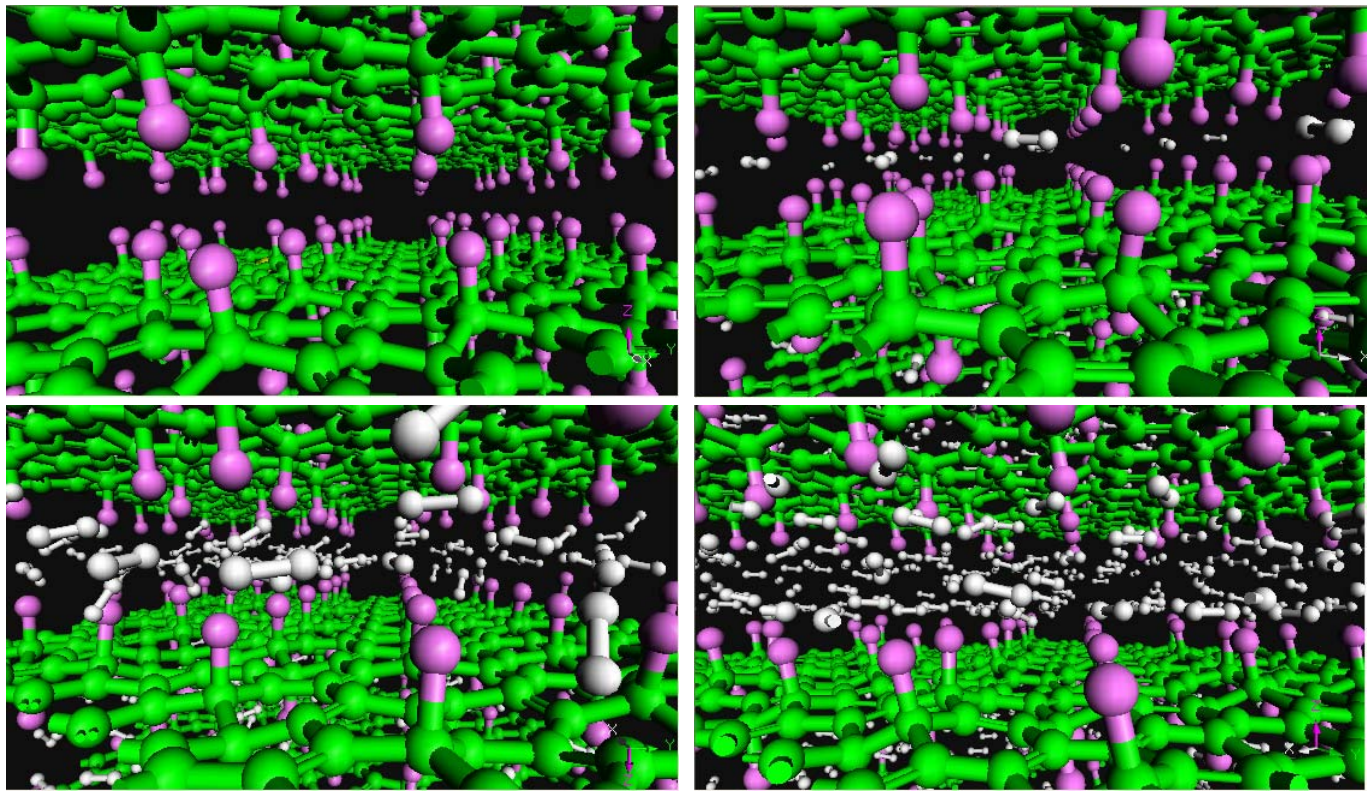
A Hydrogen Storage Material Under Investigation: F^- Anion Intercalated Graphite



ΔE = -24.3 kJ/mol H_2

F^- anion is known to interact with H_2 via charge transfer from F^- to σ^*-orbital of H_2

Ab initio MD on H_2 adsorption in F^- anion intercalated graphite at 300K



Partially fluorinated graphite destabilizes the semi-ionic C-F bonds (C-F bond length: 1.43 – 1.54 Å vs. ~1.35 Å in perfluorinated graphite

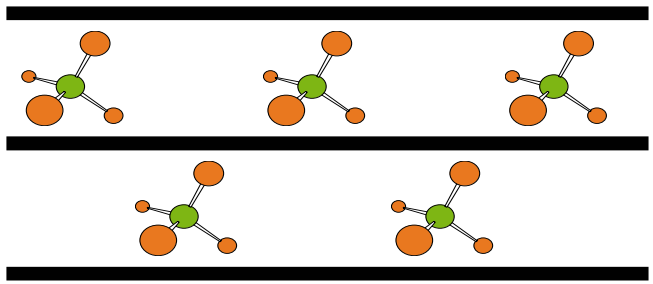
Calculation of H_2 Physisorption Energies for F^- Anion Intercalated Graphite

Complex	H_2 wt.%	d (Å)	Q_F	ΔE (kJ/mol·H_2)
$C_{32}F_8$	-	5.698	-0.659	-
$C_{32}F_8 \cdot H_2$	0.37	5.613	-0.656	-23.3
$C_{32}F_8 \cdot 2H_2$	0.74	5.602	-0.655	-19.6
$C_{32}F_8 \cdot 12H_2$	4.29	6.556	-0.657	-10.5
$C_{32}F_8 \cdot 24H_2$	8.22	7.723	-0.656	-3.6

- Significantly higher physisorption energies at low loading than other carbon-based materials at near-ambient temperatures
  - Note: Use of LDA results in a ca. 40% overestimation of the ΔE.
- C-F bonds are semi-ionic (bondlength: 1.4-1.5 Å vs. 1.35 Å in perfluorinated graphite).
- Low heat of adsorption at high loading

Graphite

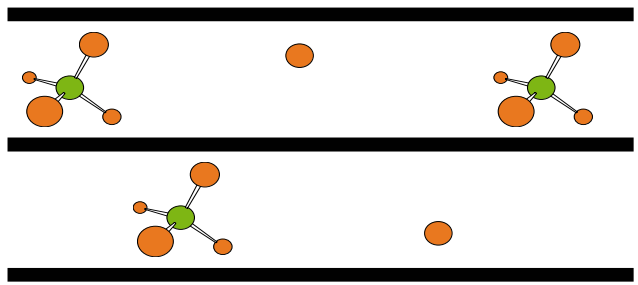
$F_2 + BF_3$



BF_4^- Intercalated graphite

heat

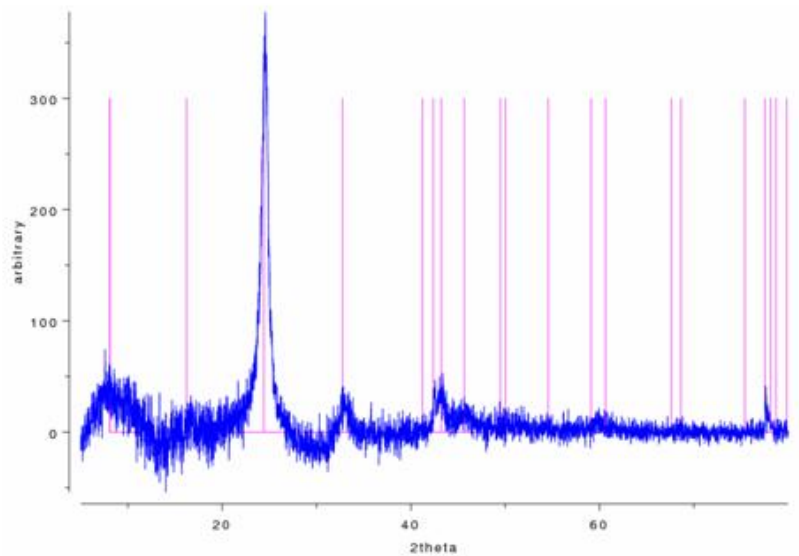
$-BF_3$



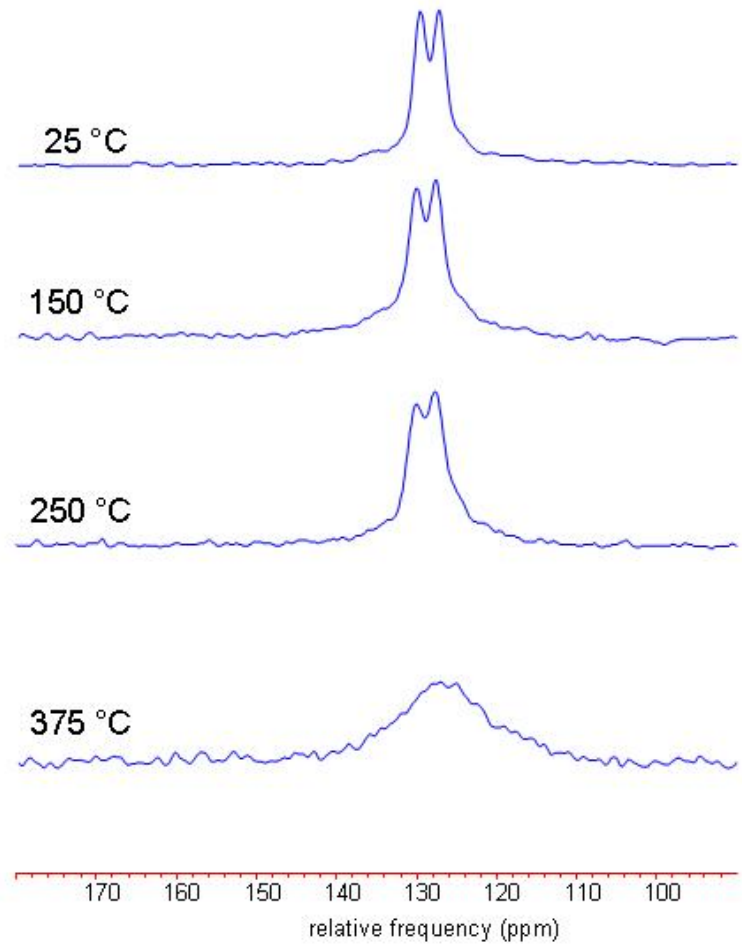
Mixed F^-/BF_4^- intercalated graphite

C_xBF_4 from
Timrex graphite

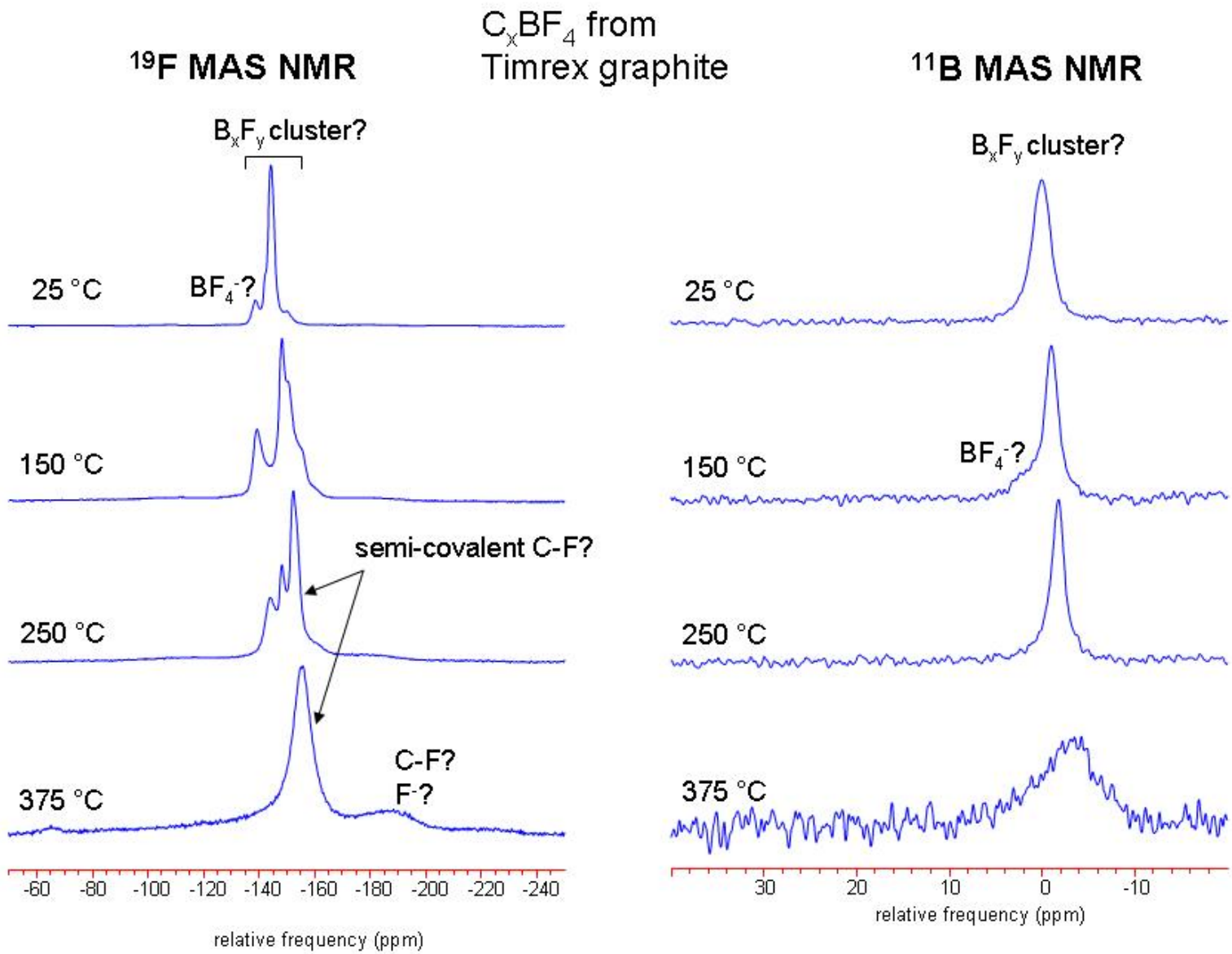
XRD 25 °C



^{13}C MAS NMR

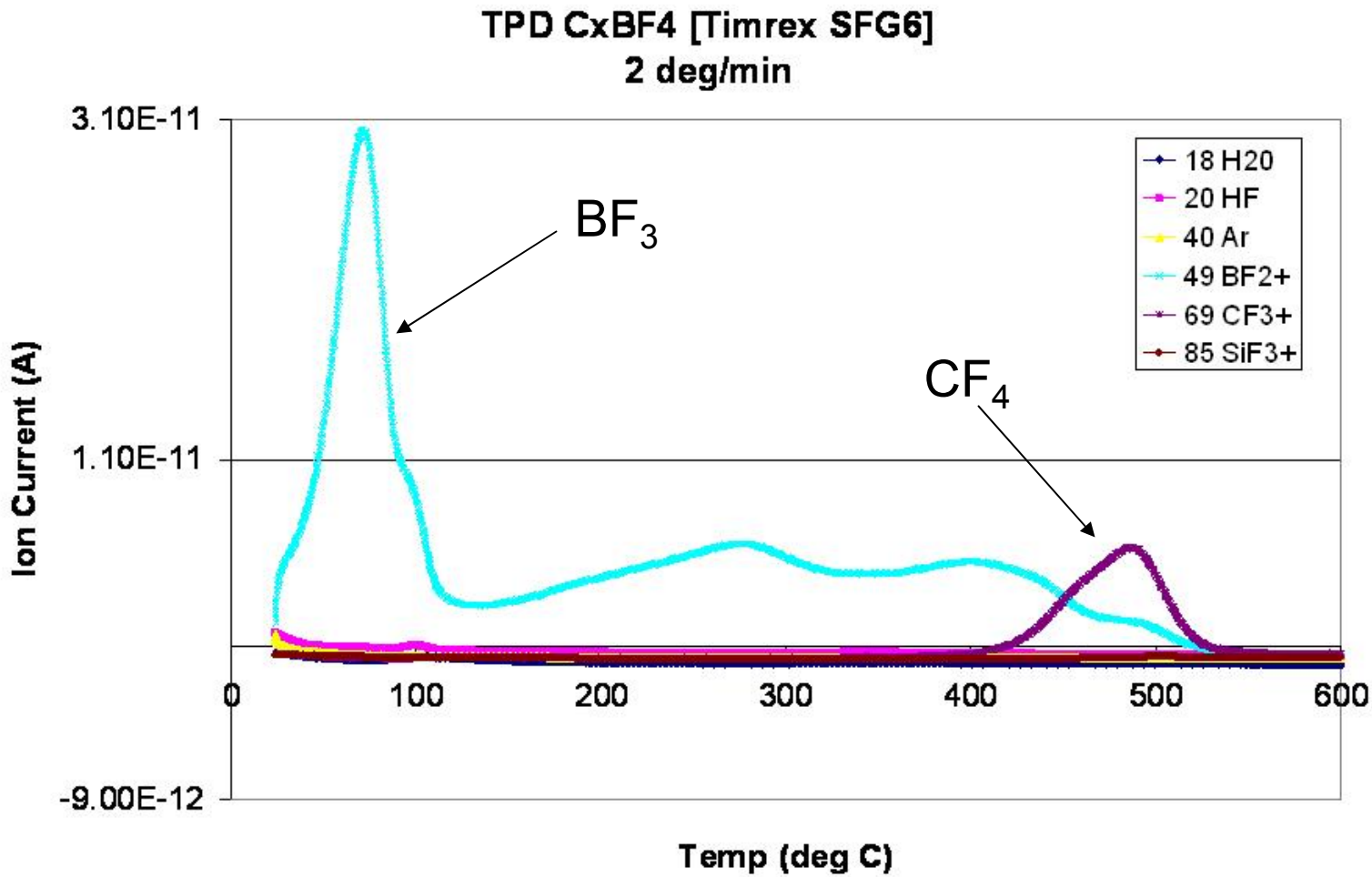


- X-ray diffraction and NMR data can be used to verify the intercalation of graphite and provide data on the degree of intercalation.



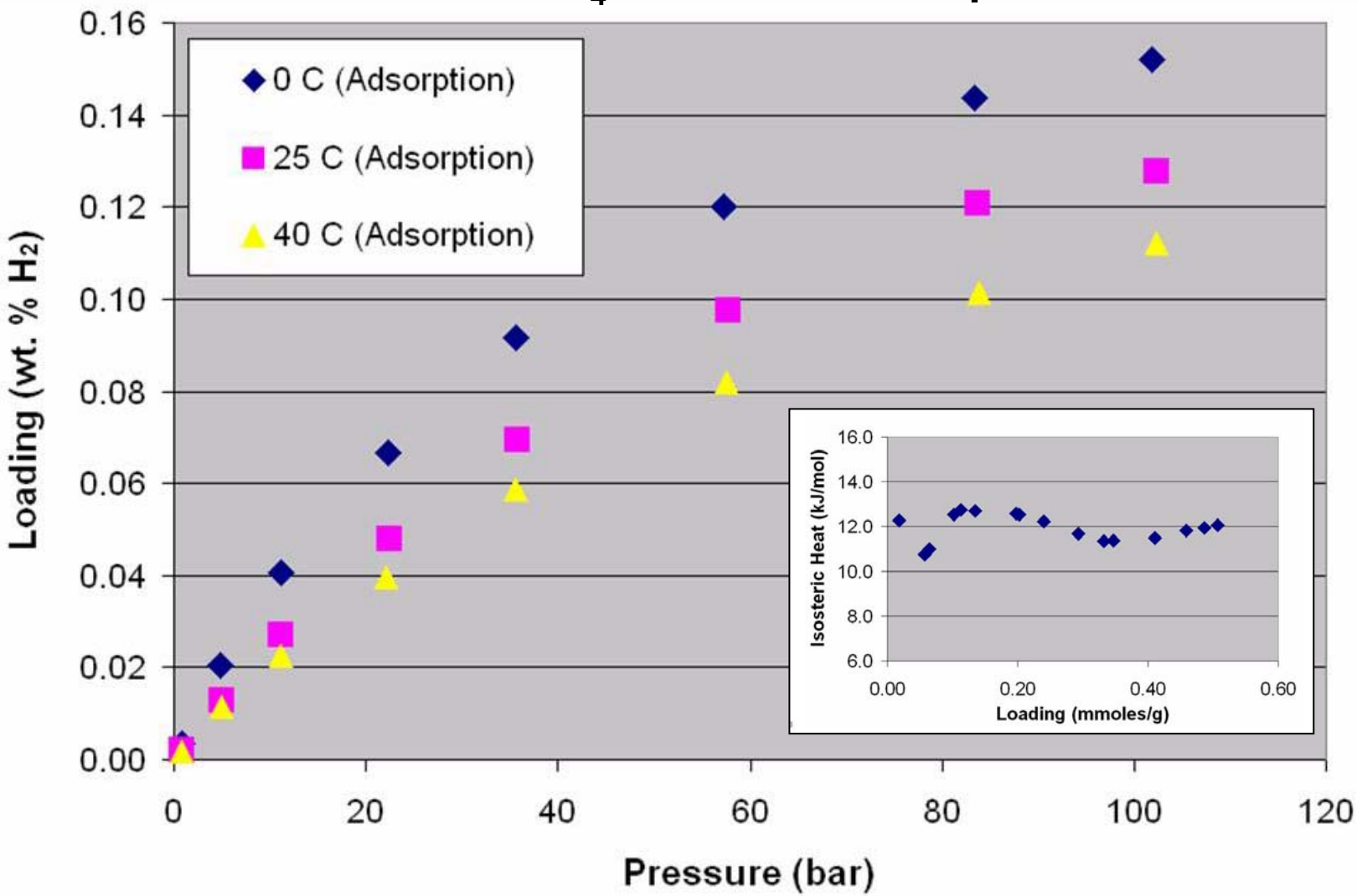
- ^{19}F and ^{11}B NMR data verify the intercalation of graphite, and provide data on the both the composition of the intercalated species and the ionic/semi-ionic/covalent nature of the C-F.

Temperature Programmed Desorption Spectrum from Heating BF_4^- Intercalated Graphite



- This technique is used to determine the decomposition temperature for the desired BF_4^-/F^- ratio.

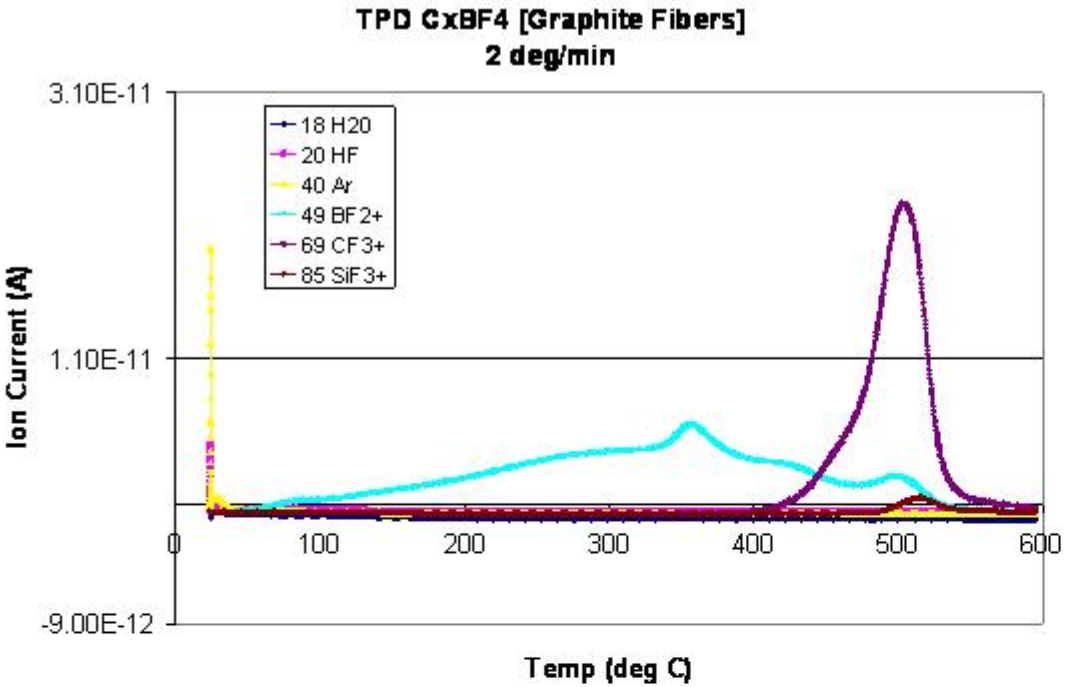
Preliminary Results: Hydrogen Isotherms (Excess Capacity) of Mixed F^- / BF_4^- Intercalated Graphite



- The heat of adsorption is ~2X activated carbon.

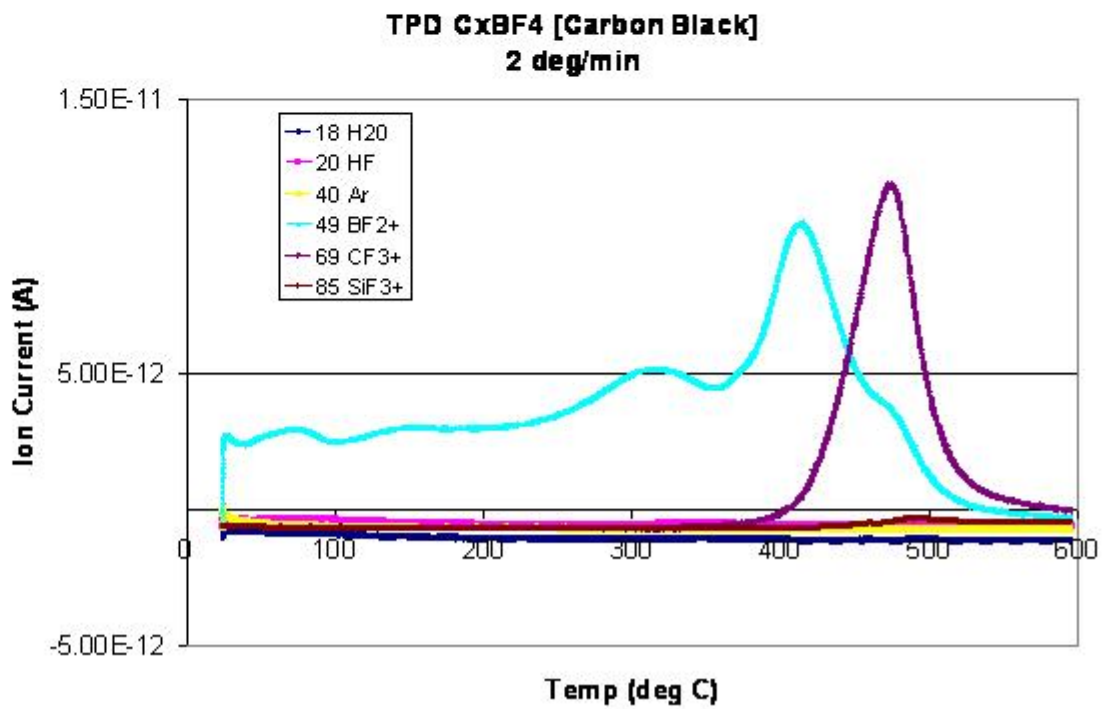
Our Challenge: Increase the Hydrogen Capacity of the F^- Anion Intercalated Graphitic Carbon Materials

- Need: Increased accessibility of hydrogen to intercalated fluoride ions (only 75 m^2/g N_2 BET surface area in experimental sample)
  - Strategy: Investigate alternative graphitic carbons with higher "edge density" and/or inherent porosity
    - Graphite nanofibers
    - Carbon nanotubes
    - Graphitized carbon black
- Need: Increased heat of adsorption of hydrogen
  - Strategy: Nitrogen doping of graphite host



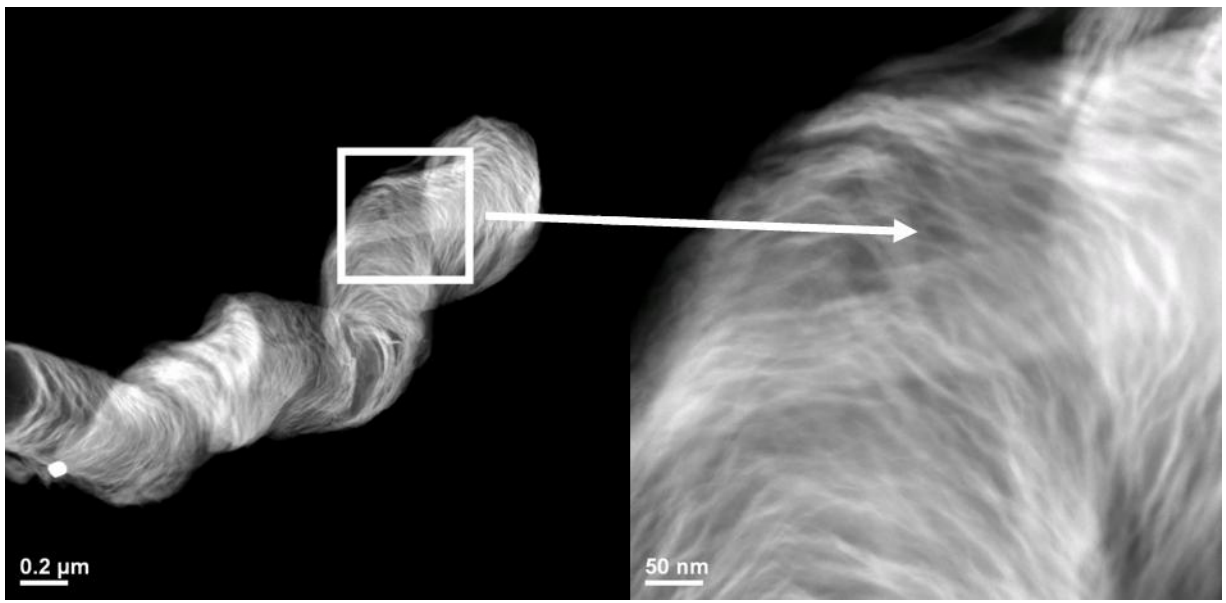
- BF_4^- intercalation complexes of graphite nanofibers and graphitized carbon black have been prepared for hydrogen storage testing.

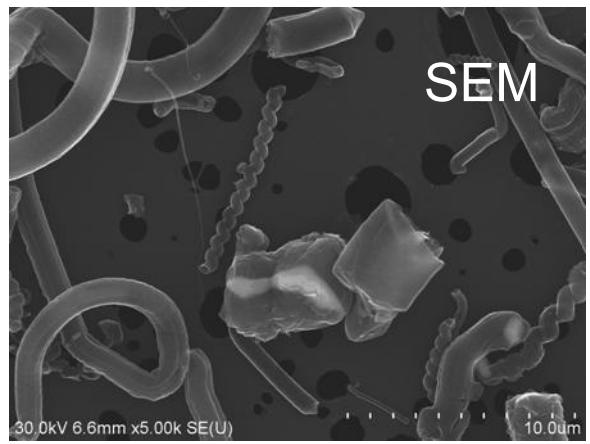
- Subtle differences in the temperature-programmed desorption spectra suggest differences in the intercalation complexes formed from these graphitic carbon "hosts."



Synthesis of N-doped carbons

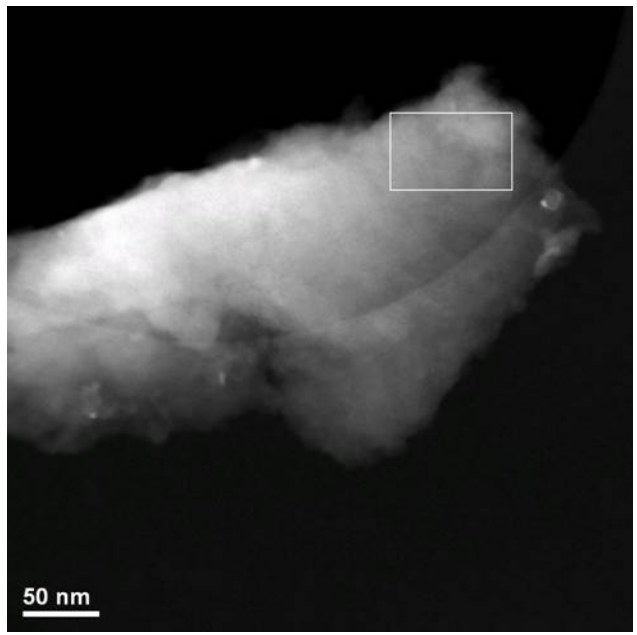
- Synthesis method is chemical vapor deposition using acetonitrile in argon and nickel catalyst; typical C:N ratio of ~$C_{26}N$.
- Particle morphology varies as hollow, large (~2μm) tubes, aggregates of tubes, and amorphous sheets.
- EELS spectra suggest C orbital hybridization similar to C in C_{60}.
- EELS spectra near N edge are not good enough to conclude anything about orbital hybridization.





Synthesis of N-doped carbons

- Synthesis method is reaction of pyridine and Cl_2 at high temperatures; typical C:N ratio of ~C_5N (reported in literature).
- EELS spectra suggest C character similar to amorphous carbon films.
- EELS spectra suggest N character similar to amorphous CN_x films.



Summary Slide – 2007 APR to Today

- **Computational study of hydrogen spillover mechanisms**
  - Status at APR: in the process of modeling every step of a H_2 spillover process on two materials
    - MoO_3 as a well-known spillover material
    - Graphitic carbon (tie-in to U. of Michigan results)
  - Progress: New understanding of several key steps in the spillover mechanism
    - Transfer of hydrogen from H-saturated catalyst particle to material
    - Migration of hydrogen atoms on graphene
    - Three publications in print, one submitted

Summary Slide (cont.) – 2007 APR to Today

- **Experimental and computational investigation of anion-intercalated graphite and nitrogen-doped graphite as hydrogen storage materials**
  - Status at APR: Initial computational modeling concluded; intercalation chemistry development beginning.
  - Progress: Additional simulations of hydrogen adsorption in graphite fluoride; first samples generated for hydrogen adsorption testing.
    - Computational proof of higher adsorption enthalpy for nitrogen-doped graphite intercalation complexes
    - Synthetic procedure developed to synthesize mixed BF_4^- / F^- intercalation complexes
    - Hydrogen adsorption testing reveals high adsorption enthalpy (~12 kJ/mol) and a surprisingly high capacity with only 75 m^2/g N_2 BET S.A.

Future Work

- FY08: Find optimal BF_4^-/F^- ratio for maximum H_2 uptake and/or heat of adsorption in intercalated graphite
- FY08: Study BF_4^-/F^- intercalation of N-doped carbon with high N levels (nominal C_5N composition); obtain hydrogen isotherm data on these materials
- FY08: Perform *ab initio* MD simulations and minimum energy path calculations on BC_3-intercalated compounds
- FY09: Introduce intercalating species, such as F^- and K^+, into BC_3 to:
  - Induce both physisorption and chemisorption
  - Enhance H_2 adsorption kinetics
- FY09: Explore the optimal concentration of intercalating species in both BC_3 and N-doped F^- intercalated graphite