Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping

-Carried in the “Hydrogen Sorption Center of Excellence ”

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06/09/2008

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Project ID # STP8

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent Complete: 60%

Budget

- Expected Total Funding
  - DOE share: $500,000
  - Contractor share: $125,000
- Funding for FY07
  - DOE Share: $100,000
  - Contractor share: $25,000
- Funding for FY08
  - DOE Share: $100,000
  - Contractor share: $25,000

Barriers and Targets

- Barriers addressed

  A. Cost.

  B. Weight and Volume.

  C. Efficiency.

  M. Hydrogen Capacity and Reversibility.
- Targets

  System Gravimetric capacity: >6%

  Volumetric capacity: >0.045 kg/L

Partners

- Interactions/ collaborations
  - NREL
  - UNC
  - Oak Ridge National Lab
  - Rice University
  - East China University of Science and Technology

Objectives of Research

- Design and synthesize carbon based materials with optimized binding energy to hydrogen molecules that will show storage capacity meeting DOE year 10 goal in hydrogen storage.
- Design and synthesize microporous carbon based materials with enhanced binding energy to hydrogen:
  - Pore size control;
  - Surface area increase;
  - Metal doping of microporous carbon materials;
  - B doping of microporous carbon materials.

Approaches

Microporous Carbon Based Materials:

- Use organic template and solution synthesis method to prepare porous carbon materials with average pore size smaller than 1 nm;
- Develop simple and scalable process for the preparation of microporous carbon materials with high surface areas;
- Utilize micropore activation to increase micropore volumes and surface area;
- Collaborate with theoretical groups to establish models that can predict the effect of pore sizes on hydrogen storage capacity;
- Incorporate dopants into various precursors for the preparation of metal doped microporous carbon materials and Boron-doped microporous carbon materials.

Technical Accomplishments

- Developed simple methods to prepare microporous carbon materials;
- Varied pore diameters to below 1nm using organic templates
- Obtained a series of samples with high surface area and high microporosity;
- Observed higher hydrogen storage capacity at 77K and 2 bar than simple estimation from surface area (Chahine rule). More interestingly, no metal and B doping of samples used in the study;
- NMR characterization confirmed the higher hydrogen storage capacity is from the high microporosity;
- Samples showed higher binding energy (8.1 kJ/mol) to hydrogen molecules.

Developed Methods to Synthesize Microporous Carbon Materials Using Organic Templates

Motivations

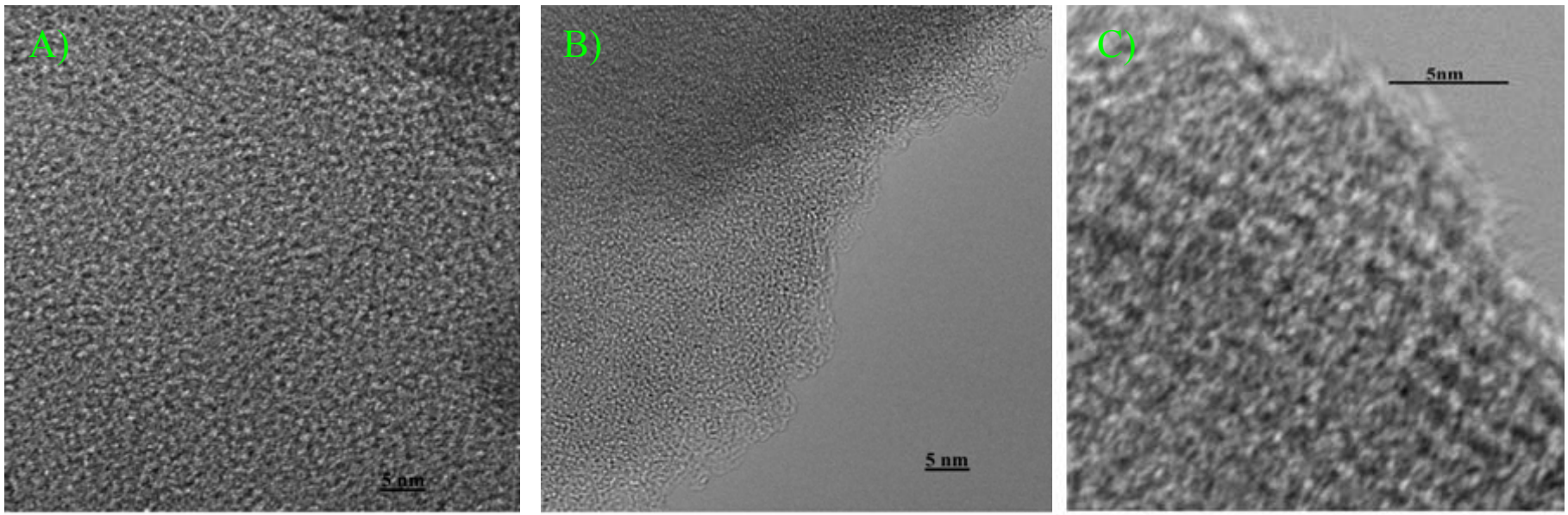
- Microporous carbon materials, such as CDC (carbide derived carbon) and Zeolite-templated carbon have demonstrated good hydrogen storage capacities (up to 3 wt% at 77K and 1 bar; 6.9 wt% at 77K and 20 bar)[1-2].
- Organic-templated porous carbon offers unique advantages compared to CDC and Zeolite-templated carbon, including the control of pore size, the flexibility in adding various dopants, the low cost in large scale synthesis and the elimination of highly toxic chemicals like chlorine and HF.
- Such materials offer a way to systematically study the effect of pore size, metal doping and B doping on the binding energy to hydrogen molecules. The ability to tune these parameters in the materials makes the design and synthesis of an ideal hydrogen storage media a possibility.

Approach

- Using various surfactant molecules to form micelles in a solution. Different surfactants will form micelles with different sizes;
- Introduce a polymerizable precursor into the solution that will interact with the outer surface of the micelles;
- Trigger the polymerization reaction to form a strong framework of polymers using micelles as templates;
- Thermally remove the surfactants;
- Graphitize the polymer at high temperature to form desired materials.

(1) G. Yushin, R. Dash,J.Jagiello, J.E.Fischer and Y.Gogotsi, Advanced Functional Materials, 16, 2288-2293 (2006).
(2) Z. Yang,Y. Xia,and R. Mokaya, JACS, 129, 1673-1679 (2007)

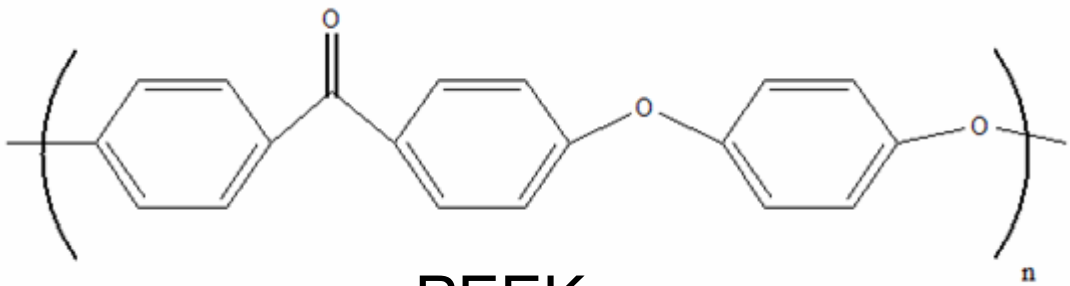
Pluronic Surfactant Templated MPC Growth



MPC's with varying pore sizes demonstrated by organic templates A) P123 B) P103 C) P84 with pore sizes: 1-2nm, 1nm, 0.6-0.8nm respectively

Micropore Content

- TEM evidence suggests scalability of pore sizes, however low BET surface areas and ^{1}H NMR data suggests inaccessible micropores;
- Micropore activation tested using molten KOH as well as CO_2 at high temperature;
- The most promising is CO_2 activation of Polyetheretherketone (PEEK) at 900C:



PEEK

PEEK Before and After Burn

Samples Sent to NREL for Testing

Samples	Micropore volume	Micropore area	External surface area
Sample A (PEEK sample treated with CO_2)	0.359 cc/g	723.517 m^2/g	57.830 m^2/g
Sample B (Templated carbon materials treated in molten KOH with C:KOH ratio being 1/3)	0.452 cc/g	902.775 m^2/g	230.132 m^2/g
Sample C (Templated carbon materials treated in molten KOH with C:KOH ratio being 1/5)	0.529 cc/g	1088.318 m^2/g	330.500 m^2/g

Samples Tested at NREL

Sample ID	SSA (m2/g)	Wt. % H2 uptake (2bar 298K)	Wt. % H2 uptake at 2bar 77K (Modified Chahine Factor)
Sample A (As Received)	690	0.019	1.72 （1.25）
Sample A (After 400C degas)	700	0.024	1.97 （1.41）
Sample B (As Received)	1080	0.037	1.90 （0.88）
Sample B (After 400C degas)	1290	0.037	2.38 （0.92）
Sample C (As Received)	878	0.035	1.67 （0.95）
Sample C (After 400C degas)	1041	0.032	1.96 （0.94）

Sample A shows much higher hydrogen uptake at 77K and 2Bar than expected from simple surface area consideration (Chahine Rule).

Additional Samples to be Tested

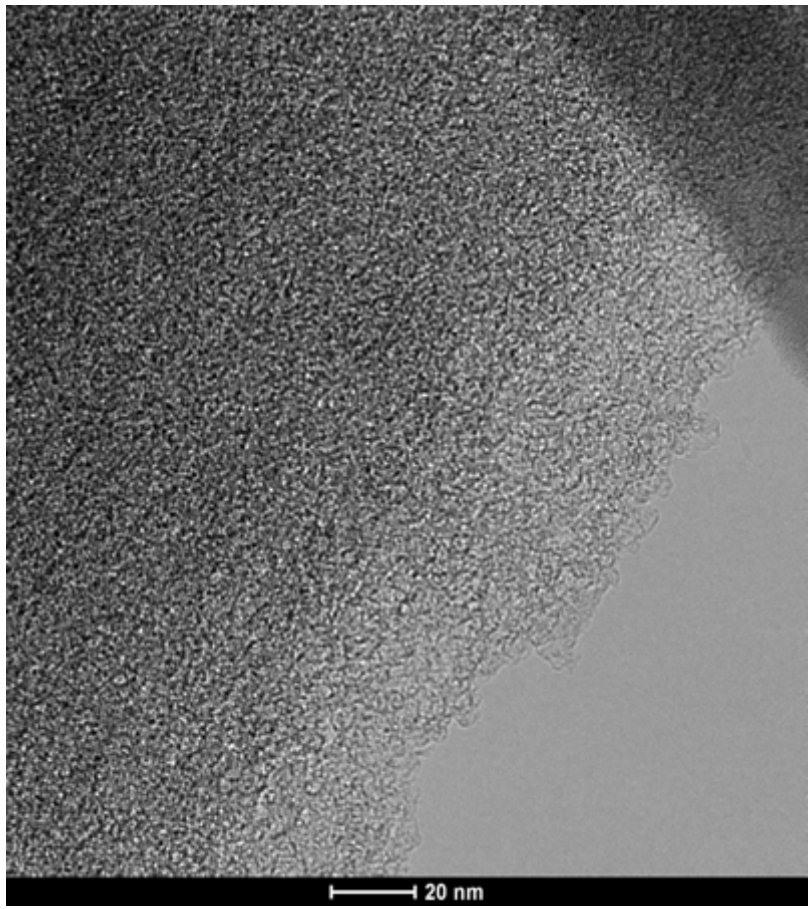
Sample ID	Weight Loss after CO_2 Activation	SSA (m^2/g)	Wt. % H2 uptake at 2bar 77K (Modified Chahine Factor)
Sample A (As Received)	5%	690*	1.72 （1.25）
Sample A (After 400C degas)	N/A	700*	1.97 （1.41）
Sample D (PEEK treated under CO_2 at 900°C for 2 hrs)	<1%	524**	To be tested
Sample E (PEEK treated under CO_2 at 900°C for 8 hrs)	26%	1027**	To be tested
Sample F (PEEK treated under CO_2 at 900°C for 24 hrs)	80%	3013**	To be tested
Sample G (PEEK treated under CO_2 at 900°C for 2 hrs)	82%	454** (Possible air leak during activation)	Characterized with NMR

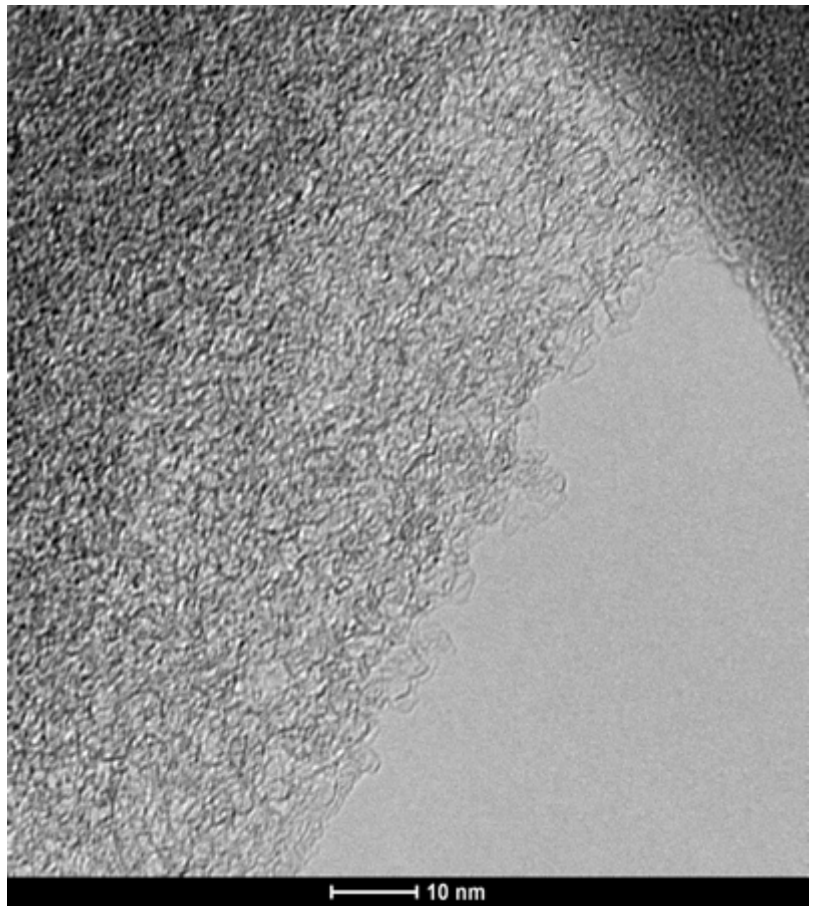
If Sample F follows the same behavior as Sample A, the hydrogen uptake can be very high since the surface area of the sample is significantly improved. This will make it an exciting material for storage.

*: Surface area Measured at NREL using N_2.

**: Surface area measured at Materialsynergy Inc. using N_2.

TEM Images of Sample F

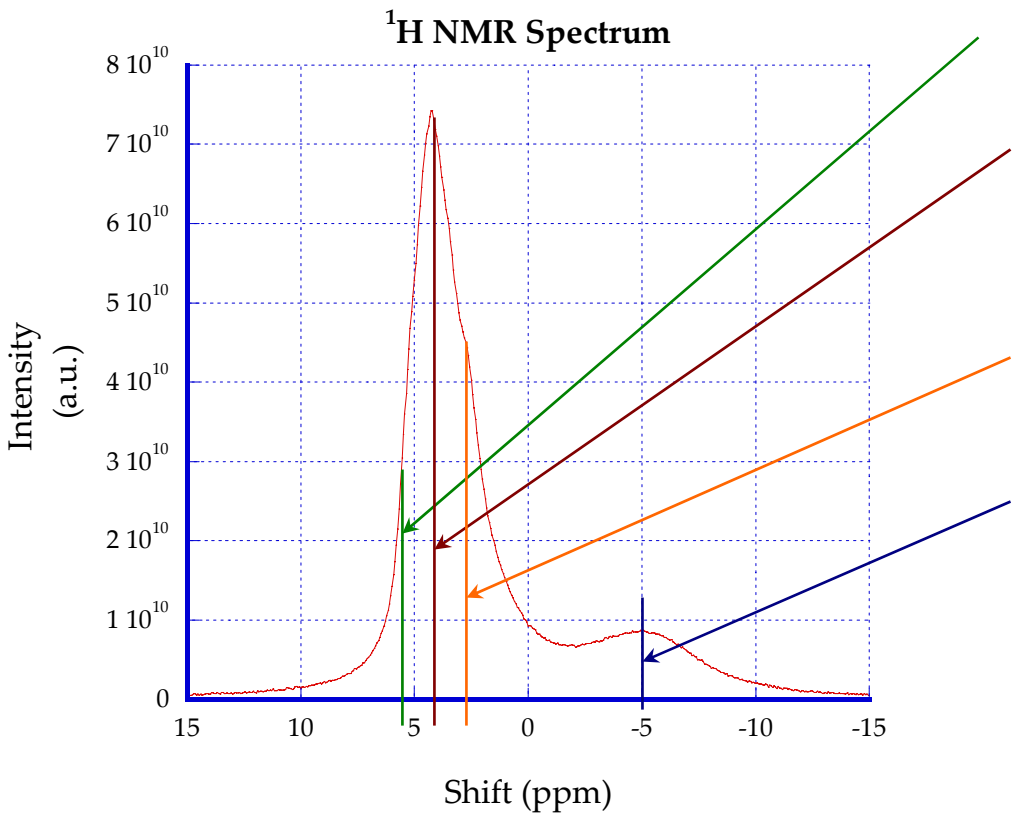




BET Surface Area = 3103m^2/g

NMR Analysis of Sample A

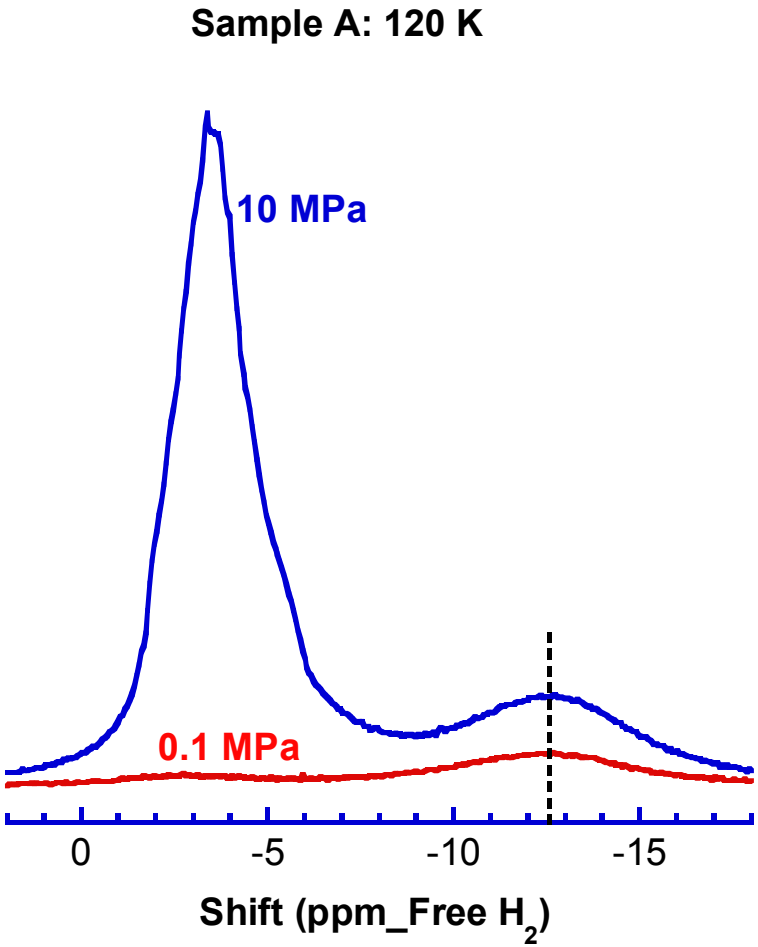
(Experiments performed at the UNC, a team member of the center)

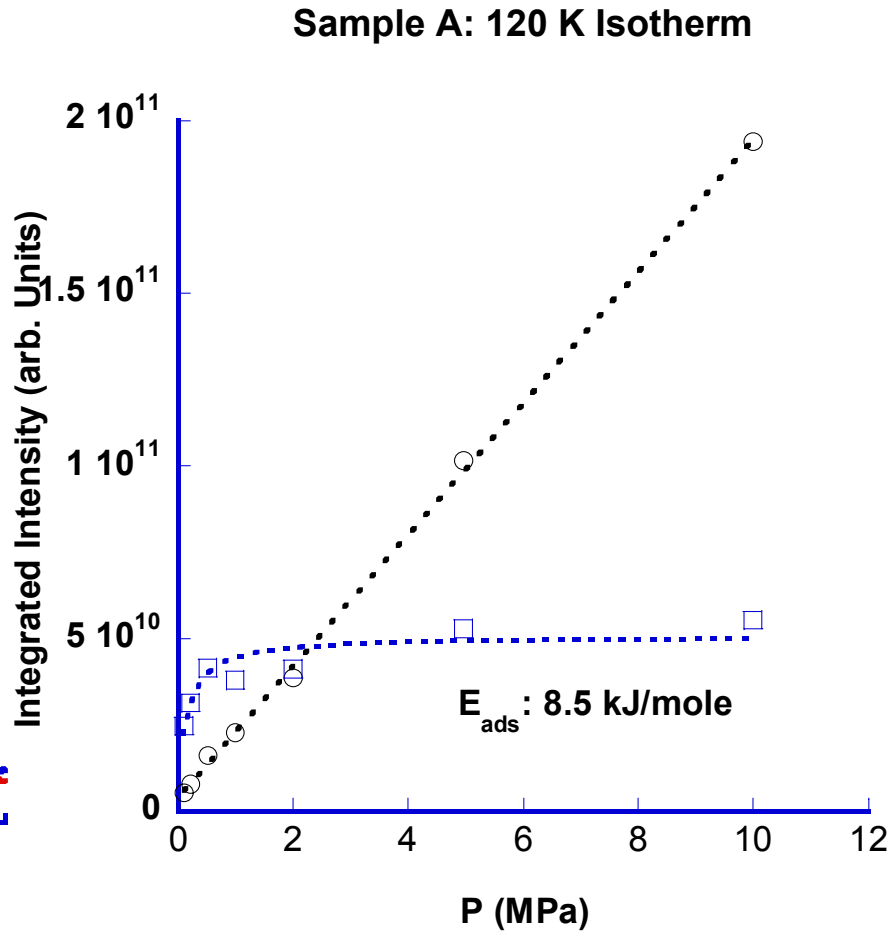


- Sample only filled ~40% of coil region, so a significant contribution from free hydrogen is expected between 4-6 ppm.
- This dominant peak is most likely *not* free gas. It almost certainly corresponds to a larger pore space, possibly voids in the sample.
- There is another peak upfield in relation to the dominant peak. This second distinct pore region would be smaller, but not much.
- **Clearly there are a significant amount of pores with a high upfield shift, indicating a pore region of $d = 1 - 3$ nm. Even though the small quantity of the sample did not allow accurate quantitative measurement of the percentage of hydrogen in the micropores, the qualitative interpretation is well supported by the data.**

NMR Analysis of Sample A

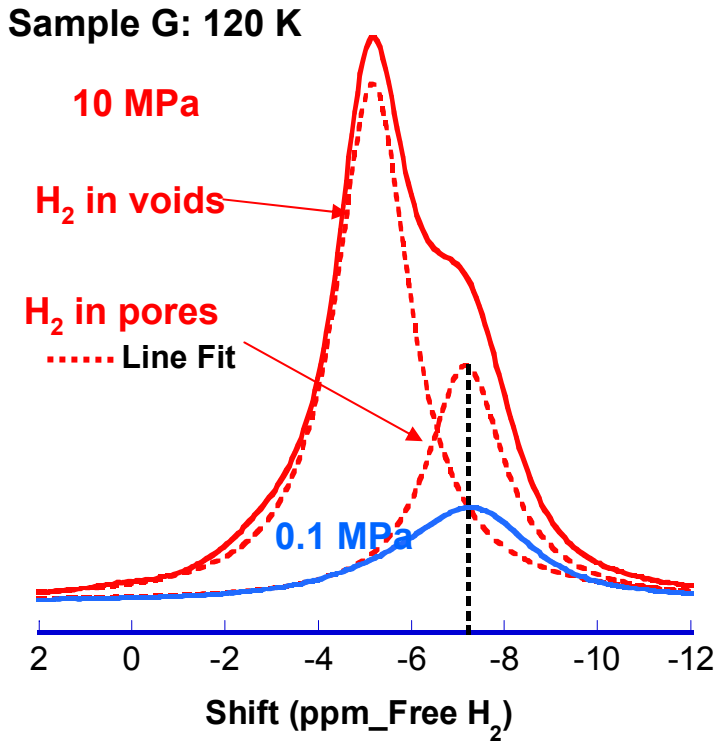
(Experiments performed at the UNC, a team member of the center)

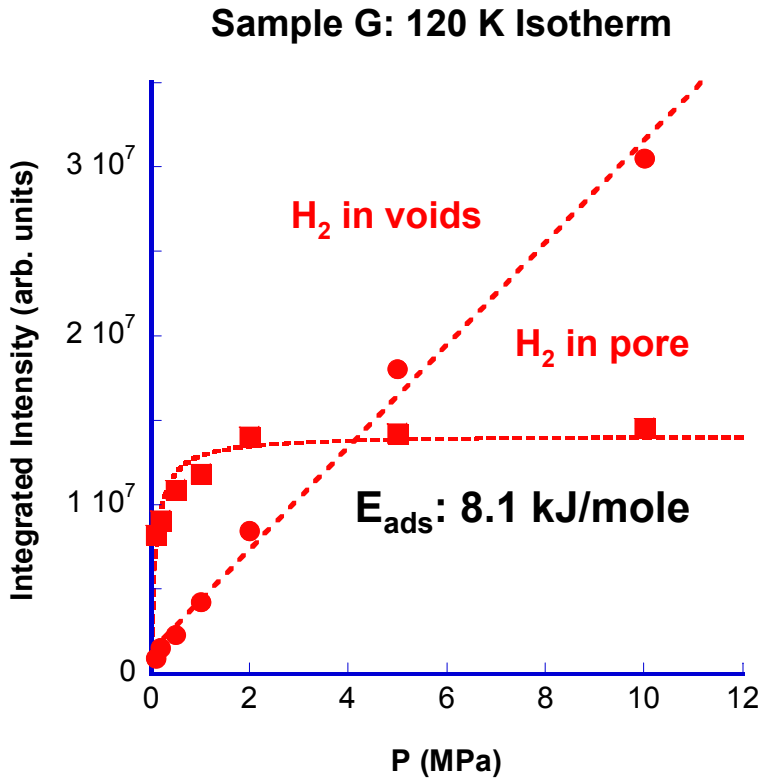




NMR Analysis of Sample G

(Experiments performed at the UNC, a team member of the center)





Sample A shows a larger shift for H2 in micro pores than samples G. However, in both cases the line does not shift with pressure indicating small pores in both samples. In addition the low temperature isotherms for both samples can be well fit with a Langmuir expression yielding a high adsorption energy of 8.1 kJ/mole expected for H2 in ideal slit pores. Currently only results from Sample A and G are available; more studies are being performed on other samples.

Challenges and Solutions in Microporous Carbon Materials

Challenges and Solutions

- **Pore size control:** The pore size control is an important issue in making a suitable material for hydrogen storage. It has been shown that the storage capacity is closely linked to the surface area related to *microporosity*. To achieve accessible micropores, activation of various materials including PEEK, Resol, and Pluronic based MPC's will be investigated.
- **Doping:** Pure microporous carbon materials already demonstrated 3 wt% storage at 77K and 1 atm, 6.9 wt% at 77K and 20 bar.[1-2] We are approaching this reported value with sample A, which has only 700 m^2/g surface area. Samples (E and F), having higher surface areas, may show much higher storage. However, the binding energies of the samples are still around 8 kcal/mol. To further improve these binding energies, doping with metal and/or boron is a necessary step.
- **Binding Energy with Hydrogen:** The key assumption of the research project is that the binding energy to hydrogen can be controlled to be higher than physisorption and lower than covalent bonding. Too low a binding energy results in low storage capacity and too high a binding energy causes problem in heat management. Through the control of pore size and doping concentration, it is highly possible that we can tune the binding energy continuously to obtain materials with optimized binding to Hydrogen. We have reached ~8 kJ/mol with our current sample measured from NMR experiments.

(1) G. Yushin, R. Dash,J.Jagiello, J.E.Fischer and Y.Gogotsi, Advanced Functional Materials, 16, 2288-2293 (2006).
(2) Z. Yang,Y. Xia,and R. Mokaya, JACS, 129, 1673-1679 (2007)

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY07 materials**	**FY08 Result**
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)	0.84 wt%*, (2 bar, 77K)	2.38 wt%*, (2 bar, 77K)
Volumetric Energy Capacity)	kWh/L	1.5		
Desorption Temperature				
Plateau Pressure				

Future Work

- Pore size control in Microporous Carbon Materials (FY08-FY09)
  - Activated PEEK material has micropore diameters in a narrow range. More systematic study planned (remainder of FY 08);
  - Systematic study on the effect of annealing temperature and duration on the surface area and microporosity of the prepared MPC materials (remainder of FY 08);
  - Develop scalable method to synthesize microporous carbon materials using organic molecules as templates. Using different surfactant molecules and different annealing temperature to control pore size distribution of the materials;
- Doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms (Main Focus for FY 09)
  - Develop a method for doping MPC from PEEK precursor to maximize H_2 uptake
  - Develop methods to use precursors containing metal atoms and Boron atoms to prepare microporous carbon with controlled doping.
  - Demonstrating the change of binding energy to hydrogen through doping. Do systematic study on the effect of pore size, surface area, micropore volume and doping level to discover the optimum binding energy for hydrogen.
  - Demonstrate the materials' storage capacity exceeds DOE system goal of 6% by weight.
- Theoretical Modeling of the Effect of Doping on Hydrogen Binding Energy (FY 09):
  - Collaboration with theory groups (Rice and Air product team) within the center to study the effect of doping on the binding energy to hydrogen and validate the prediction using experimental results. This work will start after more data is collected from a series of samples.

On-Going and Expected Collaboration

- NREL
  - Characterization of nanotubes and microporous carbon samples for their structures and hydrogen storage properties.
  - Study the effect of doping of microporous carbon on the binding energy and hydrogen storage properties.
- University of North Carolina
  - Measurement of Hydrogen binding energy as a function of pore size, metal doping and boron doping in Professor Yue Wu's Lab.
- East China University of Science and Technology
  - Collaborating with Professor Yanqin Wang's group in designing and synthesizing doped and undoped microporous carbon materials

Project Summary

Relevance:

- Understanding the effect of structure of carbon based materials on the binding energy to hydrogen and the storage capacity

Approach:

- Demonstrating that the small diameter/pore size of carbon based materials can increase the binding energy to hydrogen and improve the storage capacity.
- Controlling the pore size and volume of mesoporous carbon materials using templates.
- Using metal and boron doping on carbon materials to improve storage capacity.

Technical Accomplishments:

- Developed simple methods to prepare microporous carbon materials;
- Varied pore diameters with surfactant template to below 1nm using organic templates
- Obtained a series of samples with high surface area and high microporosity;
- Observed higher hydrogen storage capacity at 77K and 2 bar than simple estimation from surface area (Chahine rule);
- NMR characterization confirmed the higher hydrogen storage capacity is from the high microporosity
- Samples showed higher binding energy to hydrogen molecules

Proposed Future research:

- Pore size control in Microporous Carbon Materials
- Doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms
- Theoretical Modeling of the Effect of Doping on Hydrogen Binding Energy:

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