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

-Carried in the “Hydrogen Sorption Center of Excellence ”

Tom McNicholas, Anmiao Wang and Jie Liu

Duke University

05/22/2009

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID # st_29_liu

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent Complete: 80%

Budget

- Expected Total Funding
  - DOE Share: $500,000
  - Contractor share: $125,000
- Funding for FY08
  - DOE Share: $100,000
  - Contractor share: $25,000
- Funding for FY09
  - 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-Relevance

- Design and synthesize carbon based materials with optimized binding energy to hydrogen molecules that will show a storage capacity meeting DOE year 10 goal in hydrogen storage. (DOE 2010 Gravimetric Goal = 6wt.%, Volumetric Goal = 45g/L)
- Design and synthesize microporous carbon based materials with enhanced binding energy to hydrogen:
  - Pore size control;
  - High Surface area;
  - Metal doping of microporous carbon materials;
  - B doping of microporous carbon materials.

Approaches

Microporous Carbon Based Materials:

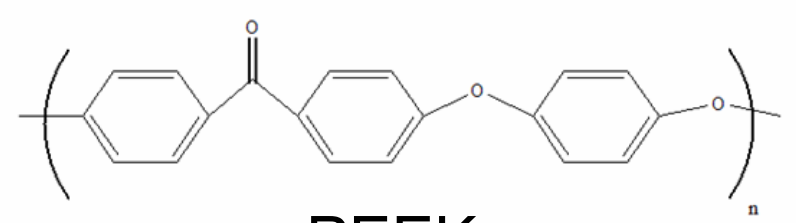
- Develop simple and scalable process for the preparation of microporous carbon materials with high surface areas and pore diameters ≤1nm ;
- Demonstrate control of degree of microporosity (pore diameter < 2nm, preferably < 1nm) rather than mesoporosity (pore diameter = 2-50nm);
- Utilize micropore activation 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 thermal treatment of poly(etheretherketone)
- Obtained a series of samples with high surface area and high microporosity;
- Demonstrated control over degree of microporosity at high surface areas;
- Observed higher hydrogen storage capacity at 77K and 2 bar than simple estimation from surface area (Chahine rule). More interestingly, no metal or B doping of samples was 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.

Background: Micropore Content

- TEM evidence of organic templated porous carbons suggests scalability of pore sizes, however low BET surface areas and H_2 NMR data suggests inaccessible micropores;
- Micropore activation tested molten KOH as well as CO_2 and Steam treatments at high temperature;
- The most promising are microporous carbons (MPC) derived from the CO_2 and Steam treatment of Polyetheretherketone (PEEK) at 900C



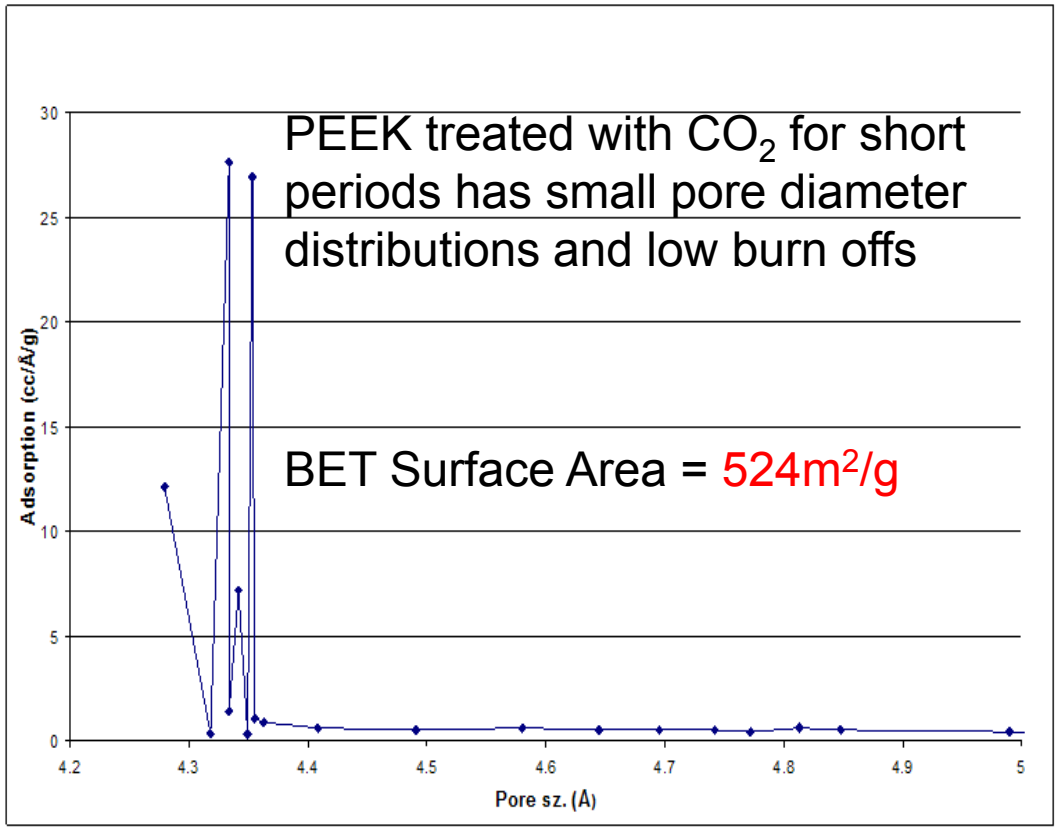
PEEK

Before Treatment

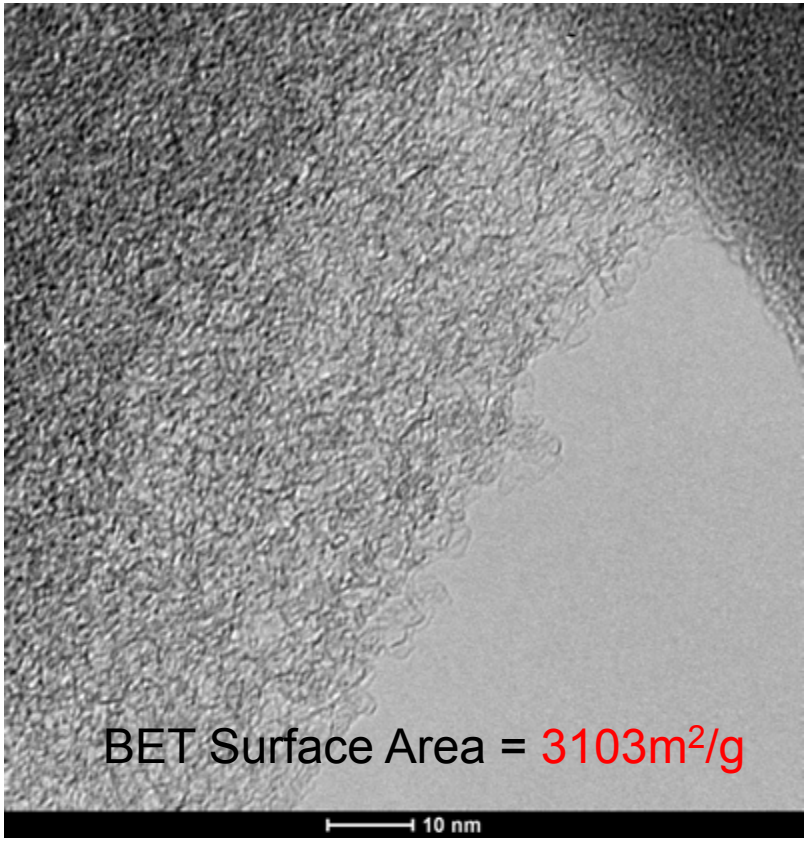
After Treatment

Technical Progress: Pore Size and Overall Surface Area under CO_2 Treatment

Absorption/Pore Size Distribution:
PEEK-CO2-9-1



TEM of PEEK-CO2-9-80

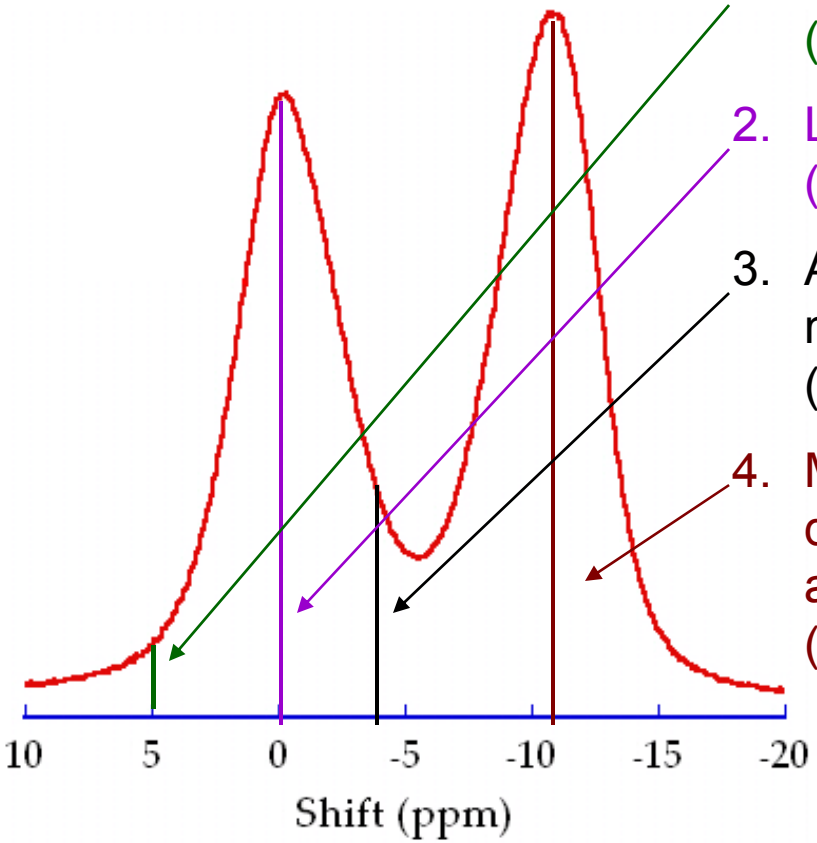


MPC surface area increase with treatment time and temperature. Longer CO_2 treatment times increase the amount of mesopores (pore diameter distribution ≥2nm)

Technical Progress:
NMR Analysis of MPC-Chemical Shifts

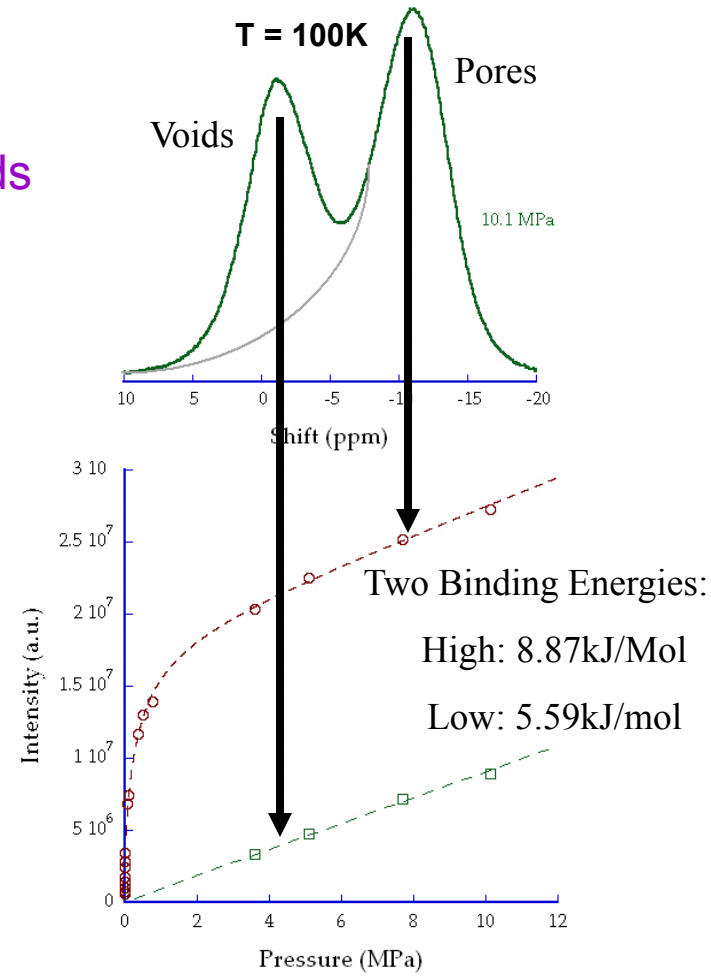
(Experiments performed at the UNC, a HSCoE team member)

PEEK-CO2-9-1



1. Free H_2 (>5ppm)
2. Larger pores/voids (0 → 5ppm)
3. Approaching mesopore range (0 → -5ppm)
4. Micropores diameter 1-3nm and below (-5 → -15ppm)

PEEK-ST-9-20

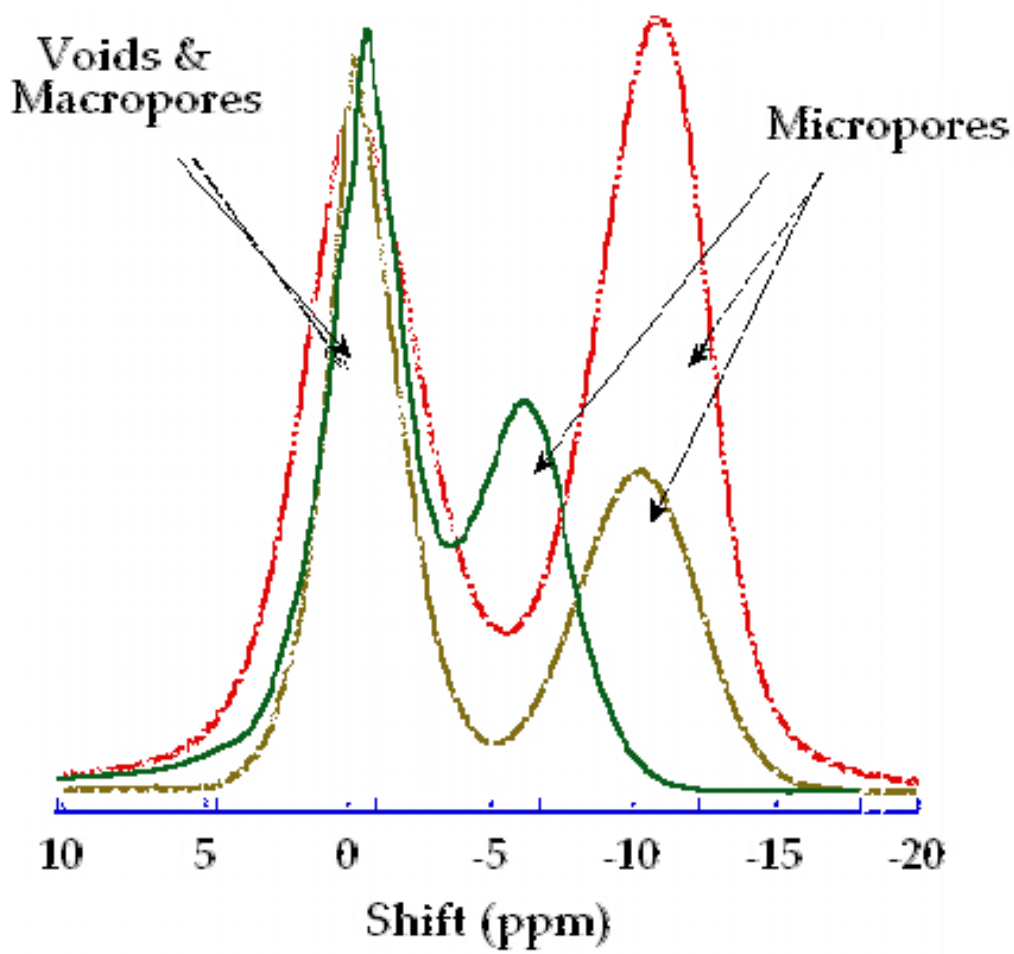


NMR used to determine the ratio of H_2 in micropores/mesopores as well as the binding energy indicate micropores have higher binding energy.

Technical Progress: Evolution of PEEK-MPC Thermally Treated Under CO_2

1. Surface area of CO_2 treated samples increase with more weight loss (Burn off);
2. At high surface area, the proportion of Hydrogen in micropores decrease ~20%.

Sample	% H_2 in Micropores	H_2 wt% (76K&2 bar)	BET SA (m^2/g)
PEEK-CO2-9-1	45	1.6	524
PEEK-CO2-9-26	37	2.2	1027
PEEK-CO2-9-80	28	3.7	3103

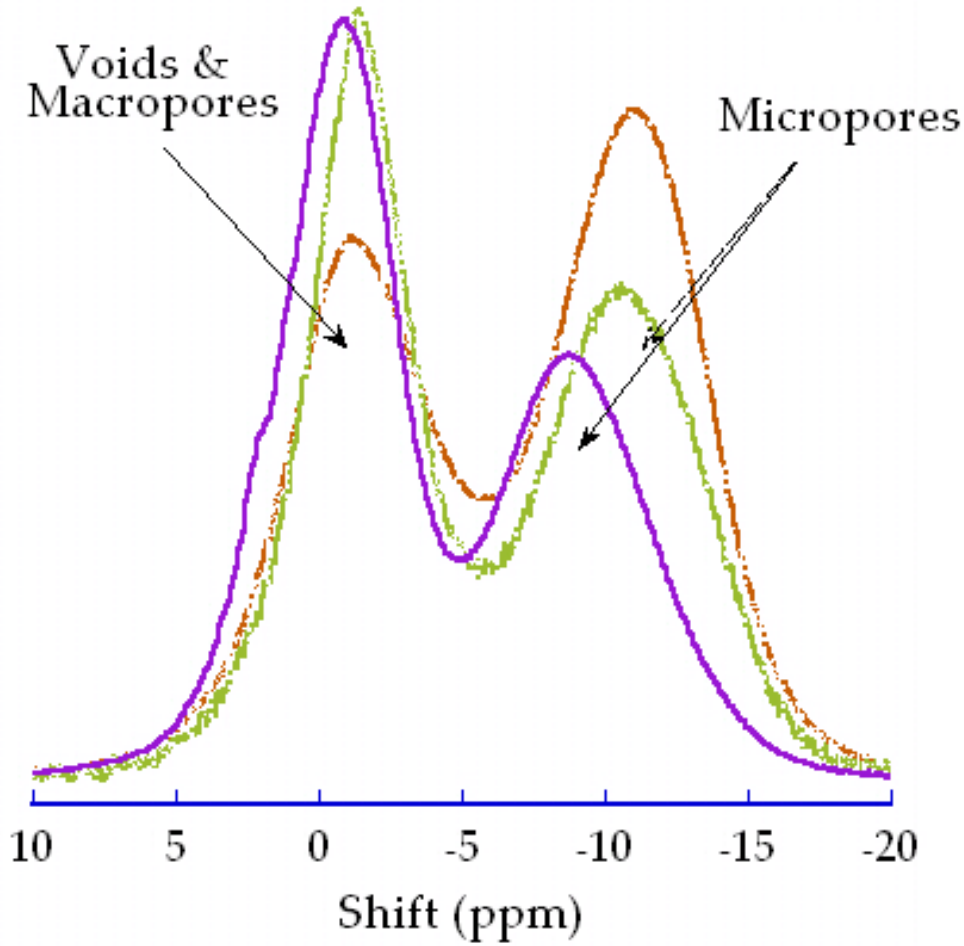


CO_2 treatment of PEEK-MPC samples produces high specific surface areas with correspondingly high H_2 storage. However, the proportion of H_2 stored by micropores decreases substantially with CO_2 enhanced specific surface area.

Technical Progress: Evolution of PEEK-MPC Thermally Treated Under Steam (Water Vapor)

1. Steam treated PEEK samples evolve higher micropore content in a controlled oxidation;
2. At high surface area, the proportion of Hydrogen in micropores only decrease ~6%.
3. Maximum excess hydrogen storage projected to be ~5-6 wt% at 77 K.

Sample	% H_2 in Micropores	H_2 wt% (76K& 2 bar)	BET SA (m^2/g)
PEEK-ST-9-20	48	2.4	1294
PEEK-ST-9-35	45	2.1	981
PEEK-ST-9-47	42	2.3	1207

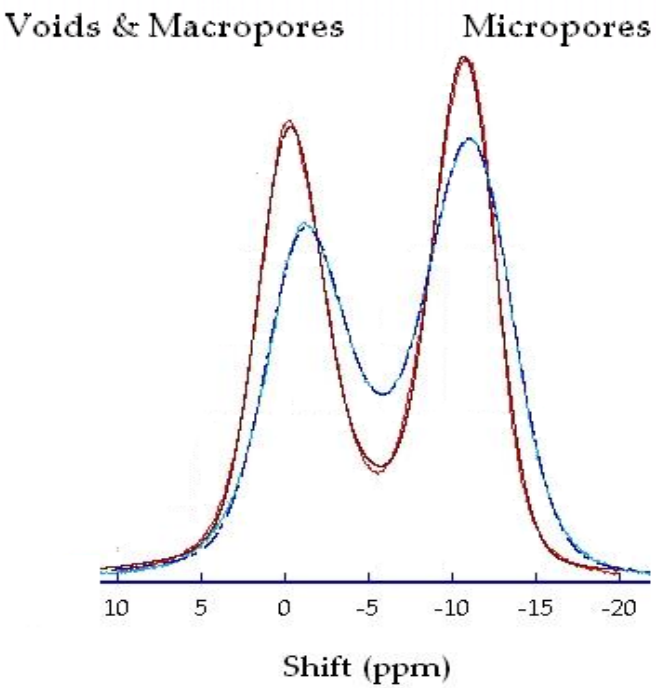


Steam treatment produces high specific surface areas, but the proportion of H_2 stored by micropores decreases much less than in CO_2 treated samples. This indicates steam conserves microporosity while increasing BET SA better than CO_2.

Technical Progress: Comparison of CO_2 and Steam Treated PEEK-MPC's

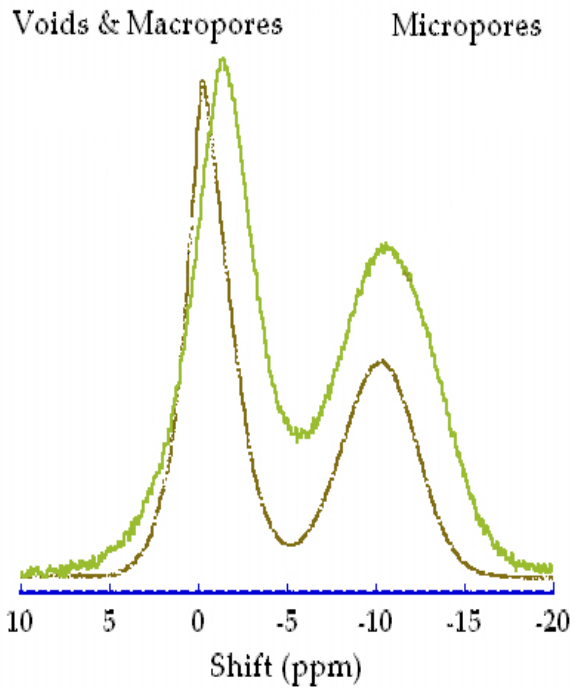
Similar Microporosities

Sample	% H_2 in Micropores	H_2 wt% (76K&2 bar)	BET SA (m^2/g)
PEEK-CO2-9-1	45	1.6	524
PEEK-ST-9-20	48	2.4	1294



Similar Surface Areas

Sample	% H_2 in Micropores	BET SA (m^2/g)
PEEK-CO2-9-26	37	1027
PEEK-ST-9-35	45	981

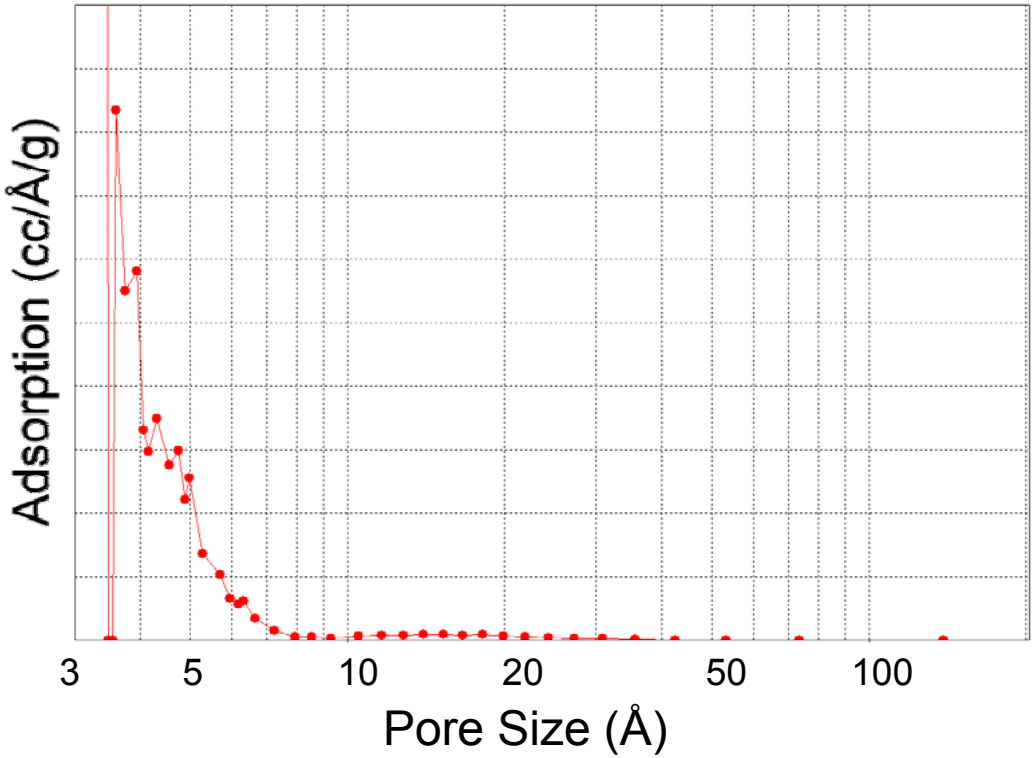


At similar specific surface areas, Steam activated MPC's display higher H_2 sorption and have significantly more H_2 stored in micropores.

Technical Progress: Pore Size Conservation and H_2 Uptake of High Surface Area Steam Derived MPC

PEEK derived MPC show remarkably selective binding to H_2 and >99% available net capacity assuming heating to 80C and 3bar for fuel cell

H_2-Absorption Isotherm: Pore Size Distribution of PEEK-ST-9-70 (1956m^2/g)



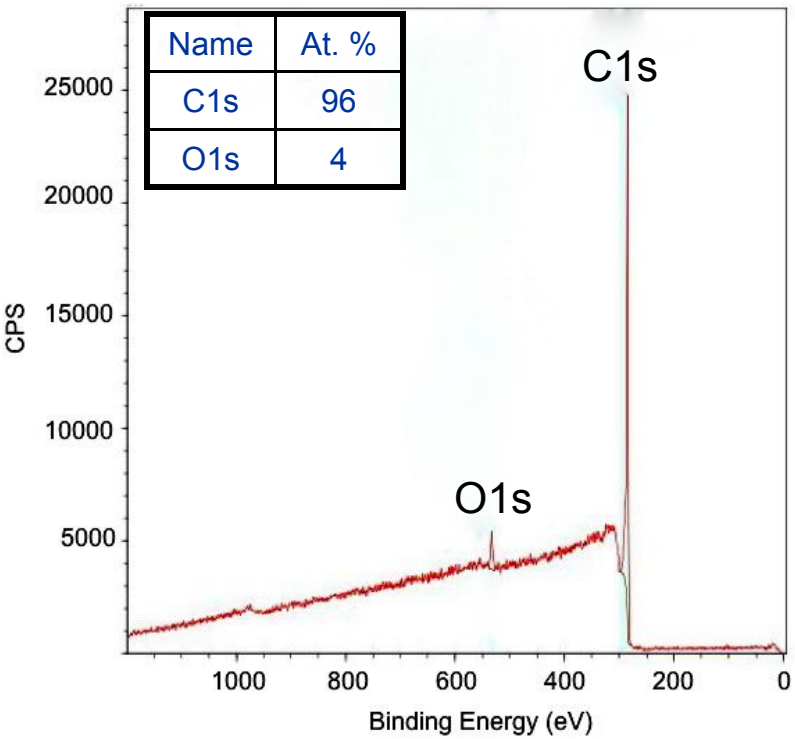
Sample	SSA (m^2/g)	H_2 Wt% (*)
AX-21	3300	3.0
PEEK-ST-9-35	1031	2.1
PEEK-ST-9-80	1658	2.5
PEEK-ST-9-91	2368	2.9
PEEK-ST-9-96	2802	2.9
PEEK-CO_2-9-51	1572	2.6
PEEK-CO_2-9-59	1915	2.8
PEEK-CO_2-9-65	2149	2.8

*Measurements Taken at 2bar, 75K

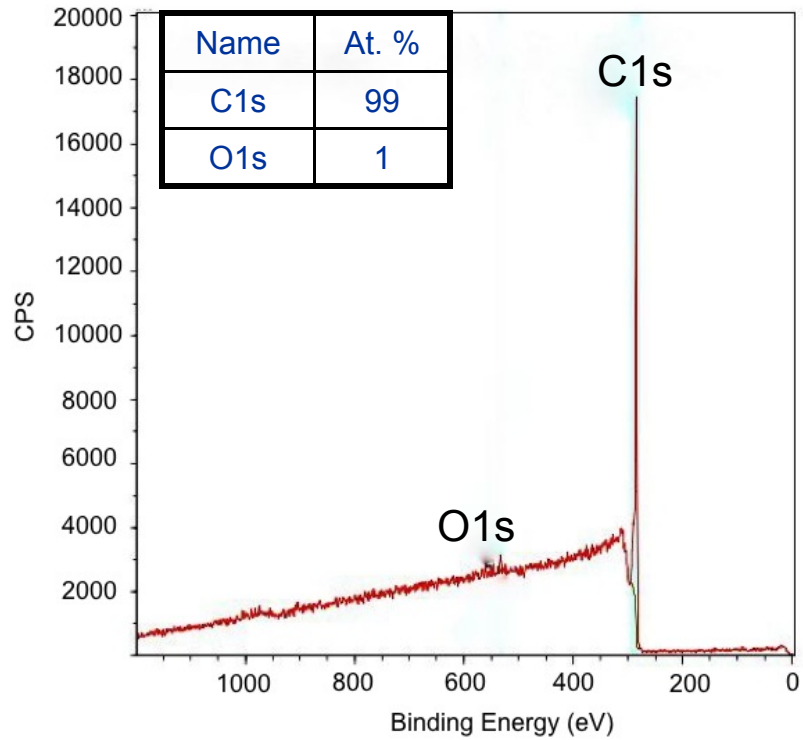
Steam activated MPC's conserve microporosity even at high surface areas. As such, they consistently display high H_2 uptake at 75K and 2 bar. Several samples demonstrated close to 3% hydrogen uptake. This micropore conservation helps to improve both H_2 binding energy as well as sample density (0.7-1g/ml).

Technical Progress: XPS of Pure Carbon (Low Oxygen Content) MPC From Steam v CO_2

PEEK-CO_2-9-80



PEEK-ST-9-91



The PEEK-MPC produced using both CO_2 and Steam are pure carbon materials with very low Oxygen content even after significant thermal treatment. This indicates the successful production of desired pure carbon materials with high surface areas.

Material	BET SA (m^2/g)	H_2 wt.% §	Volumetric Capacity (g/L)	% H2 in Micropores ǂ
PEEK-CO2-9-1	524	1.6	11	45
B/C[1]	780	~1.6 (at77K,1.2bar)		
PEEK-CO2-9-5	700	2.0	14	
CMK-1[2]	1788	2.19 (77K,1bar)		
PEEK-CO2-9-26	1027	2.2	15	37
PEEK-ST-9-47	1207	2.3	16	42
PEEK-ST-9-20	1294	2.4	17	48
PEEK-ST-9-70	1956	3.0	18	
AX-21[3]	3300	~3.0 (77K, 2bar)		
PEEK-CO2-9-80	3103	3.7	26	28
Corncob[4]	3500	~5 (at 77K, 20bar)		

1. T.C. Mike Chung; DOE Annual Merit Review Presentation, June 2008
2. Gao, L.; International Journal of Hydrogen Energy 33 (2008) 116 – 123
3. Measured at NREL
4. Pfeifer, P.; RC 1 TT Presentation

DOE 2010 Gravimetric Goal = 6wt.%, Volumetric Goal = 45g/L

Volumetric data calculated from H_2 sorption data and average density of MPC samples = 0.7g/ml*

ǂ from NMR done at UNC-CH

§measurements done at 77K, 2bar unless otherwise indicated

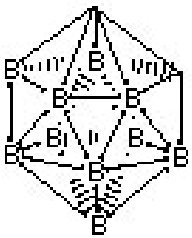
The PEEK-MPC have significant H_2 storage capabilities compared to other pure carbon materials

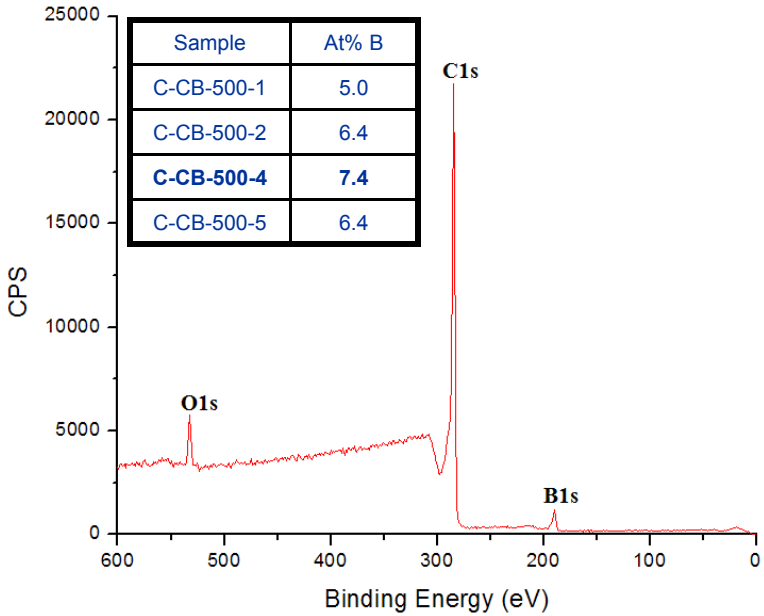
Technical Progress: B-Doping of MPC

Motivation: B doping of our high surface area MPC's (>3000m^2/g) will help improve the binding energy and improve upon its storage capacity (3.7wt%, 26g/L at 77K, 2bar).

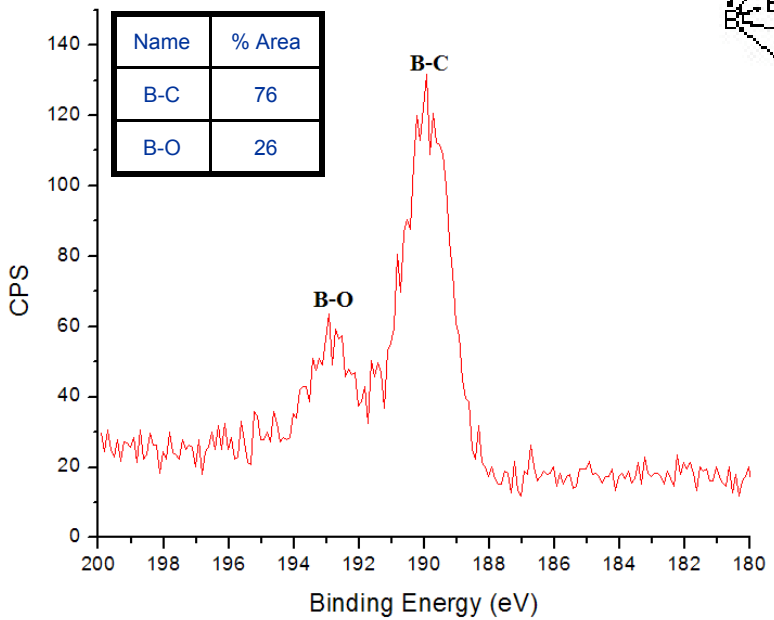
Preparation: These samples are prepared by thermally treating a mixture of high surface area MPC and carborane sealed under vacuum. This helps to decrease the oxygen content and effectively form C-B bonds.

O-Carborane ($C_2H_{12}B_{10}$)





Sample	At% B
C-CB-500-1	5.0
C-CB-500-2	6.4
C-CB-500-4	**7.4**
C-CB-500-5	6.4



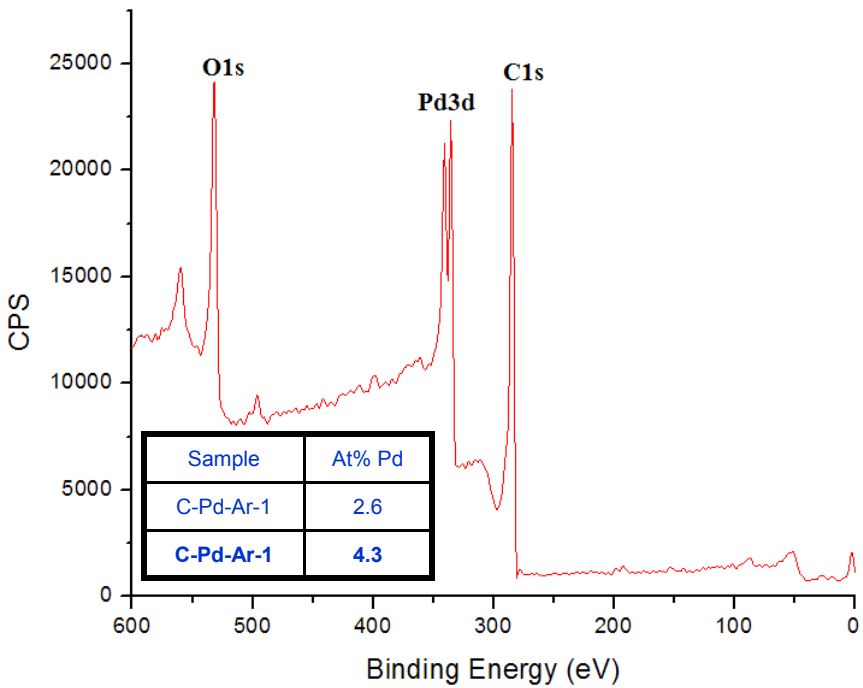
Name	% Area
B-C	76
B-O	26

Using vacuum heating and Carborane mixed with MPC's, boron contents of up to 7.37 At% (6.6 wt%) were achieved with predominately desired B-C Structure. This sample is presently under analysis.

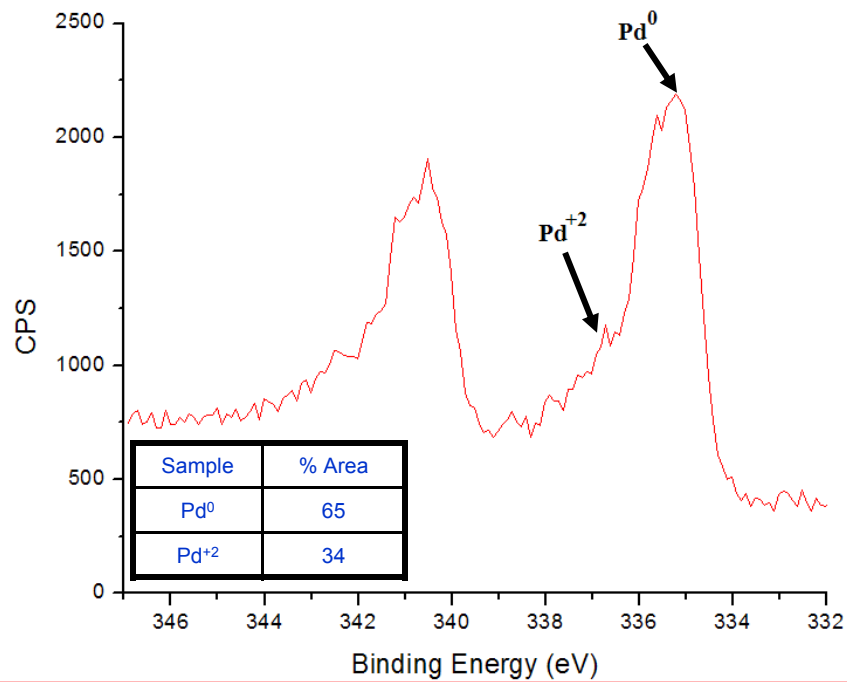
Technical Progress: Pd-Doping of MPC

Motivation: Pd doping is implemented for "spillover" studies using MPC's.

Preparation: Mixtures of Pd salt (H_2PdCl_4) and MPC's are subjected to reduction by formaldehyde, thus forming Pd particles on the MPC structure.



Sample	At% Pd
C-Pd-Ar-1	2.6
C-Pd-Ar-1	**4.3**



Sample	% Area
Pd^0	65
Pd^{+2}	34

Using liquid reduction and H_2PdCl_4 mixed with MPC's, Pd contents of up to 4.35At% were achieved. However, the oxygen content may still be too high. This sample is presently under analysis.

Challenges and Solutions in Microporous Carbon Materials

- **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*. Using PEEK thermally treated with steam, which produces samples with a larger number of micropores per unit surface area as compared to those produced with CO_2, we will map the dependence of H_2 storage relative to microporosity and surface area.
- **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 have achieved up to 3.7wt% at 77K and 2bar with PEEK-CO2-9-80. The binding energies of the analyzed samples are still around 8 kcal/mol. To further improve these binding energies, doping with metal and/or boron is a necessary step. Thus far, we have demonstrated up to 4.35 At% Pd and 7.37 At% B; these samples are presently under analysis.
- **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 problems 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)

Future Work

- Pore size control in Microporous Carbon Materials (FY09-FY10)
  - Systematic study on the effect of annealing temperature on the surface area and microporosity of the prepared MPC materials (remainder of FY 09);
  - Map the dependence of H_2 storage capacities on microporosity and surface area.
  - Help calibration of H_2-NMR (UNC-CH)
- Doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms (Main Focus for FY 10 and beyond)
  - Demonstrate variability in Doping level for B and Pd
  - Tune our methods for doping PEEK derived MPC with Pd and B to maximize H_2 uptake
  - Demonstrating the change of binding energy to hydrogen through doping. Do systematic studies 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.
- Remaining Issues
  - Scale up and cost reduction
  - Effect doping has on structure of MPC; does doping affect pore volumes, diameters or accessibility.
  - Increasing H_2 sorption beyond simple surface area/pore diameter dependence; surface area limitation is ~3000m^2/g for this material

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**	**FY09 Result**
Specific Energy	kWh/kg (wt. % H_2)	2.0 (6 wt.%)	0.84 wt%*, (2 bar, 77K)	2.38 wt%*, (2 bar, 77K)	3.67wt% (2 bar 77K)
Volumetric Energy Capacity	kWh/L	1.5	0.196 ǂ	0.55 ǂ	0.855ǂ
Desorption Temperature					
Plateau Pressure					

ǂCalculated assuming Hydrogen energy density =33.3kWh/kg (120MJ/kg) as indicated in the "Overview of Storage Development DOE Hydrogen Program" from 2000 and material density of 0.7g/ml.

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 microporous carbon materials using thermal treatment.
- Using metal and boron doping on carbon materials to improve storage capacity.

Technical Accomplishments:

- Developed simple methods to prepare microporous carbon materials;
- Varied number of micropores in PEEK derived MPC;
- 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
- Scalable Pd and B doping was achieved

Proposed Future research:

- Temperature dependence of pore size control in Microporous Carbon Materials
- Further doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms
- Analysis of doped samples

Jie Liu
(919)660-1549
j.liu@duke.edu

On-Going and Expected Collaboration

- NREL
  - Characterization of 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