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

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Project ID # ST081

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent Complete: 100%

Budget

- Expected Total Funding
  - DOE Share: $500,000
  - Contractor share: $125,000
- Funding for FY09
  - DOE Share: $100,000
  - Contractor share: $25,000
- Funding for FY10
  - DOE Share: $0.00
  - Contractor share: $0.00

Barriers and Targets

- Barriers addressed

  A. Cost.

  B. Weight and Volume.

  C. Efficiency.

  M. Hydrogen Capacity and Reversibility.
- DOE 2015 Targets

  System Gravimetric capacity: >5.5%

  Volumetric capacity: >0.0450 kg/L

Partners

- Interactions/ collaborations
  - NREL
  - UNC
  - Caltech
  - 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 storage capacity meeting DOE year 10 goal in hydrogen storage. (DOE 2015 Gravimetric Goal = 5.5 wt.%, Volumetric Goal = 40 g/L)
- Design and synthesize microporous carbon based materials with enhanced binding energy to hydrogen:
  - Pore size control;
  - High Surface area;
  - High packing density.

Overview of Projects

Project 1: Small Diameter Single Walled Carbon Nanotubes (SWNTs) for Hydrogen Storage (Project terminated and materials down selected):

- Synthesized small diameter SWNTs for the study of hydrogen storage properties;
- Measurement results did not show improved hydrogen storage capacity as a function of diameter;
- The cost of materials is too high to be widely usable as hydrogen storage materials;
- Material down selected due to problems related to cost and other problems.

Project 2: Synthesis of Microporous Carbon Materials using Organic Templates (Project terminated and materials down selected):

- Studied the use of organic templates for the synthesis of microporous carbon materials. The advantage over the use of inorganic templates, such as zeolites, is that no solid need to be removed after the formation of the materials;
- Discovered that the control of pore sizes using such an approach is difficult to achieve.

Project 3: Synthesis of Microporous Carbon Materials using Polymeric Precursors:

- Discovered a method for low cost synthesis of microporous carbon materials from simple polymer precursors (Polyetheretherketone (PEEK)) though high temperature activation under CO2 and/or water vapor;
- Hydrogen uptake at 77K and 2bar can be as high as 3.7% wt%;
- Excess Hydrogen uptake at high pressure is >5 wt%;
- Compare with AX21, the density of the materials is much higher, ~0.7 g/ml, making the material desirable for high volumetric hydrogen uptake;
- Samples send to UNC for NMR characterization, the measurement results is consistent with measurements from NREL and Caltech teams.
- One of the material studied (PEEK-CO2-9-80) achieved 88% of the DOE 2015 target in volumetric energy density at around 20bar and 77K.

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;
- Collaborated with NREL and Caltech to perform high pressure measurements at 77K.

Technical Accomplishments

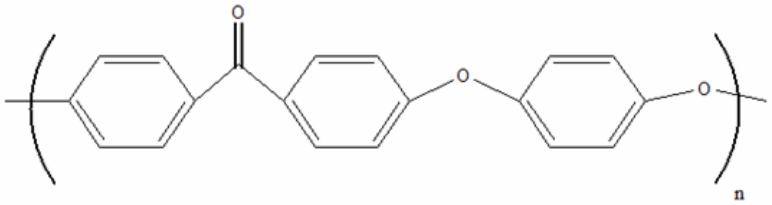
- Developed simple methods to prepare microporous carbon materials;
- Varied pore diameters to below 1nm using thermal treatment of poly(etheretherketone)
- Obtained a series of samples with high surface area and high microporosity;
- Demonstrated control over degree of microporosity at high surface areas;
- Observed higher hydrogen storage capacity at 75.6K and >20 bar;
- NMR characterization confirmed the higher hydrogen storage capacity is from the high microporosity;
- Samples showed >5.0% uptake of hydrogen at 75.6K and >20 bar. The measurement were confirmed by center partners at both NREL and Caltech;
- The same materials showing high hydrogen uptake also showed high density of the materials, 0.7-1 g/ml, showing promising potential for high volumetric uptake.

Summary of Materials Synthesized and Studied

1. Single walled carbon nanotubes:
    1. Purification is a major problem;
    2. Cost too high for large scale application;
    3. Down Selected.
2. Double Walled carbon nanotubes:
    1. Sample prepared to verify a reported high hydrogen uptake value;
    2. Did not observe any enhancement of hydrogen storage capacity as reported by literature.
    3. Down selected.
3. Zeolite templated microporous carbon materials:
    1. Sample prepared to verify a reported high hydrogen uptake value;
    2. Encountered problem related to template removal. Can not completely remove the zeolite from the products;
    3. The use of HF to remove zeolite is not safe.
4. Surfactant templated microporous carbon materials:
    1. Discovered that the pore structure is difficult to control. Samples synthesized by the method did not show high hydrogen uptake at 77K and 2 bar;
    2. Down Selected.
5. PEEK derived microporous carbon materials:
    1. Studied a long list of materials from PEEK precursors activated under different temperature and gas environments. See the next page for a table of materials studied and compared to other carbon materials;
    2. Some of the samples showed high hydrogen uptake at 77K and 2bar
    3. PEEK-CO2-9-80 showed high hydrogen uptake at 77k and 2bat (3.7 wt%) and at ~20 bar (>5 wt%)
    4. Density of the materials is high: 0.7 g/ml to 1.0 g/ml;
    5. Good candidate for high volumetric hydrogen uptake.

Background: Microporous Carbon Materials from Polymer Precursors

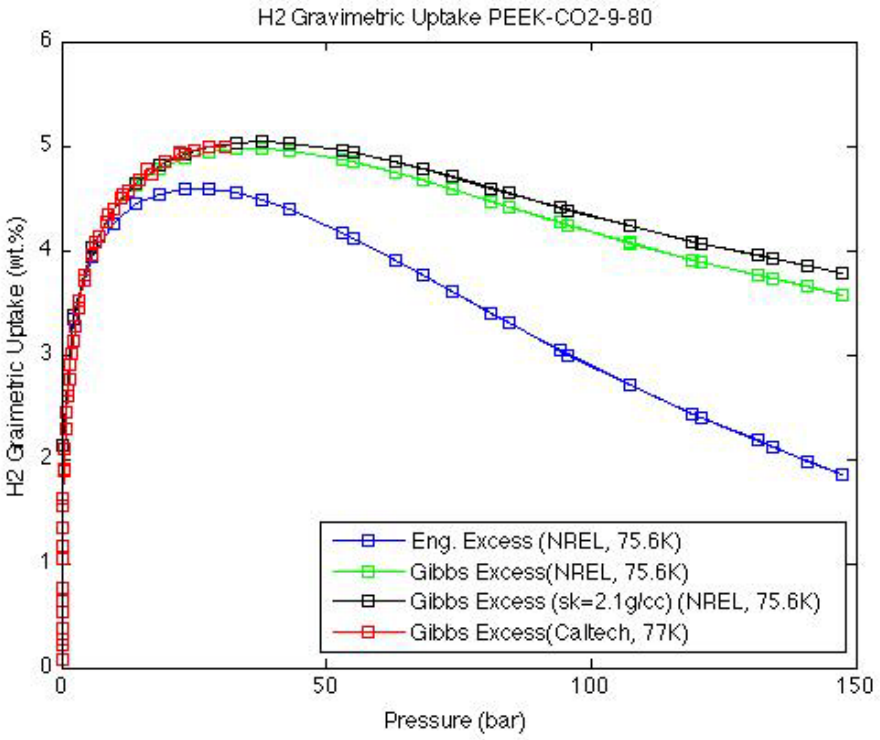
- TEM evidence suggests scalability of pore sizes, however low BET surface areas and H_2 NMR data suggests inaccessible micropores;
- The most promising are microporous carbons (MPC) derived from the CO_2 and steam treatment of Polyetheretherketone (PEEK) at 900°C

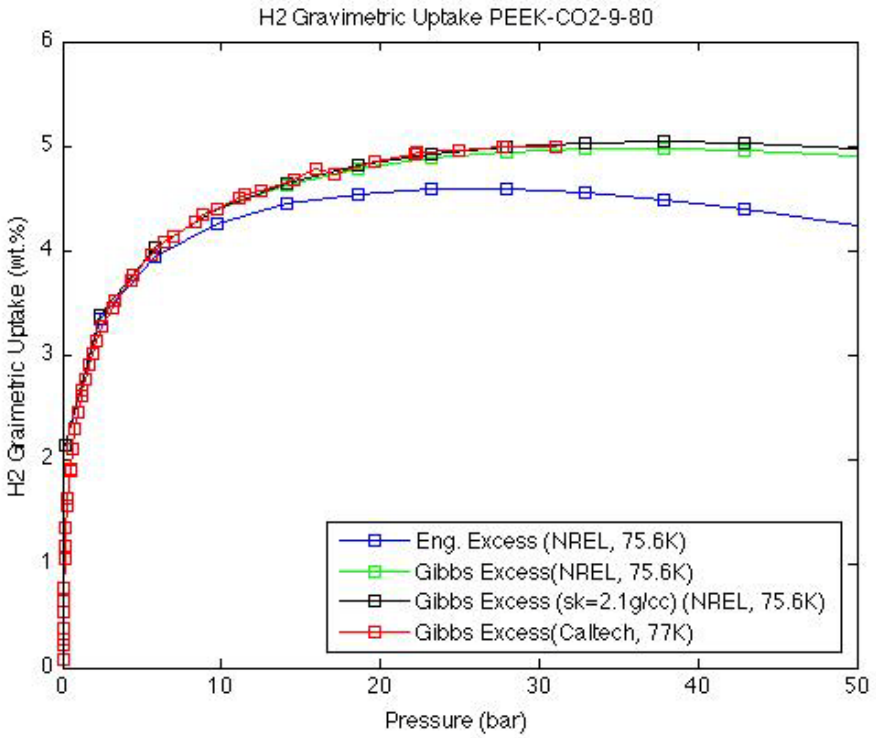


PEEK

A)

Technical Progress: High Pressure Measurements at 77K





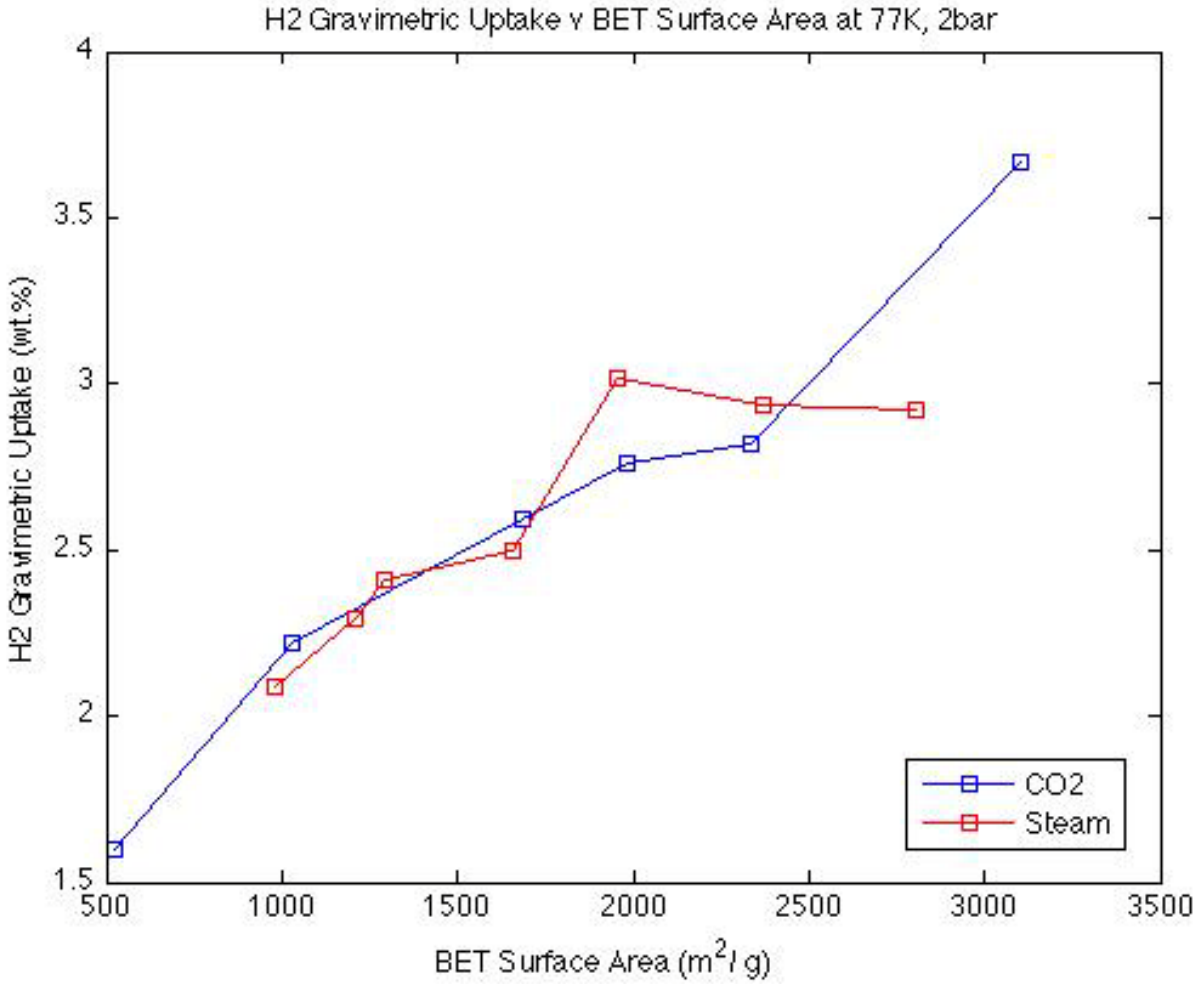
High pressure measurement of the hydrogen uptake at both NREL and Caltech showed ~5 wt% at ~20 bar and 75.6K.

Technical Progress: Detailed Study on the Sample (PEEK-CO2-9-80)

Measurement	Data
N_2 BET Surface Area (NREL)	3259m^2/g
N_2 BET Surface Area (Material Synergy)	3103m^2/g
Excess H_2 Gravimetric Uptake (NREL)	3.7 wt.% (77K,2bar)
Excess H_2 Gravimetric Uptake (Caltech)	5.1wt.% (77K, 40bar)
Excess H_2 Gravimetric Uptake (NREL)	5.0wt.% (77K, 40bar)
Total H_2 Gravimetric Uptake (UNC)	5wt.% (100K, 100bar)
N_2 Differential Pore Volume Measurements (NREL)	D=1.2, 1.35, 1.8 and 2.5nm V=0.1, 0.11, 0.07 and 0.06$cm^3/Å/g$ (respectively)
N_2 Cumulative Pore Volume (NREL)	~1.7cm^3
H_2 Binding Energy (UNC)	~8kJ/mol
H_2 Binding Energy (Caltech)	8.12kJ/mol
Density (Duke)	~0.7cm^3/g

Detailed study performed on the sample showing high hydrogen uptake. The high pressure measurements at NREL and Caltech agree well with NMR study at UNC.

Technical Progress: Relationship of BET Surface Area and Hydrogen Uptake at 77 K and 2 Bar



At low BET surface area, the hydrogen uptake per unit surface area is higher. However, as the BET surface area increases, the average hydrogen uptake per unit surface area becomes lower.

Technical Progress: Studied Effect of Combined Water Vapor and CO2 Activation

Name	Burning off(%)	Pore volume（cm^3/g）	H2 uptake At 77k and 2 bar
PEEK-CO2-ST-9-8/11	62	N/A	2.46
PEEK-CO2-ST-9-8/14	74	N/A	2.50
PEEK-CO2-ST-9-8/18	80	N/A	2.60
PEEK-CO2-ST-9-15/14	94	N/A	2.90
PEEK-ST-CO2-9-15/10	76	N/A	2.83

In order to further increase the hydrogen uptake, we studied the effect of combining water and CO2 activation for the controlling of pore structures in MPC. Several samples made with both CO2 and water activation steps combined. More systematic studies are ongoing.

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	5.0 (75.6K, 20 bar)	~35	
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

Summary Table

On-Board Hydrogen Storage System Targets

(**Data is based on material only, not system value)

Storage Parameter	Units	DOE 2015 System Target	FY07 materials	FY08 Result	FY09 Result
Specific Energy	kWh/kg (wt. % H_2)	1.8 (~5.5 wt.%)	0.84 wt%*, (2 bar, 77K)	2.38 wt%*, (2 bar, 77K)	5.0wt% (20 bar 75.6K)
Volumetric Energy Capacity	kWh/L (kg H_2/L system)	1.3 (0.04)	0.196 ǂ	0.55 ǂ	1.155ǂ (0.035)
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.

Technical Accomplishments:

- Developed simple methods to prepare microporous carbon materials;
- Varied number of micropores in PEEK derived MPC;
- 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
- High Pressure measurements showed >5 wt% hydrogen uptake at 75.6K and 20bar.
- Obtained sample showing volumetric energy capacity close to 88% of the DOE 2015 target.

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

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
- Caltech
  - Collaborating with Professor Channing Ahn's group in high pressure measurement of hydrogen uptake in microporous carbon materials