IV.C.1d Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping

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Objectives

Design and synthesize sorbent materials with optimized binding energies which meet DOE 2010 hydrogen storage targets. Specific efforts include:

- Pore size control
- Surface area increase
- Metal doping of microporous carbon materials
- Boron-doping of microporous carbon materials

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(G) Materials of Construction
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets

Enhanced Hydrogen Storage in Microporous Materials:

This project focuses on developing a microporous carbon with controlled pore diameter, pore volume and chemical doping. The goal of this research is to develop a microporous carbon with the appropriate binding energies to meet the DOE 2010 hydrogen storage targets of:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

TABLE 1. Progress Towards Meeting Technical Targets for Storage

Characteristic	Units	2010 System Storage Targets	Duke 2008 Materials Status
wt%		6% the weight of the whole system	>6% the weight of sorption materials at 120 K, 10 MPa (from NMR measurements)
Surface Area	m^2/g	NA	3,103 (by BET)
Binding Energy	kJ/mol	N/A	8.1

NMR – nuclear magnetic resonance
BET – Brunauer-Emmett-Teller
NA – not available
N/A – not applicable

Accomplishments

- Developed simple methods that could produce inexpensive hydrogen storage materials with specific energy densities above the DOE 2010 target of 6 wt% system weight.
- Demonstrated that pore diameters could be varied to below 1 nm using organic templates to enhance dihydrogen binding past mesoporous limits.
- Obtained microporous carbon (pore diameter 1-3 nm) from poly(ether ether ketone) (PEEK) activation; this is important because porous carbons with a high degree of microporousity have been proposed to be best for H_2 storage.
- Obtained a series of samples with high surface area ($>3,000\ m^2/g$) and high microporosity; (previous surface area $\leq 250\ m^2/g$) by Chahine rule, this should correspond to >6 wt% H_2 storage which surpasses the DOE 2010 goal.
- Observed higher hydrogen storage capacity (>3 wt%) at 77 K and 2 bar than simple estimation from surface area (Chahine rule). More interestingly, no metal or boron-doping was used in the study. With this doping, it is hoped that we will meet or surpass the DOE 2010 target of 6 wt%.
- H_2-NMR characterization confirmed the higher hydrogen storage capacity is from the high

microporosity, supporting previous claims that microporous carbons are best for H_2 storage; the measurement at 10 MPa showed >6% storage at 120 K, thus surpassing the DOE 2010 Goal of 6 wt%.

- Samples showed higher binding energy (8.1 kJ/mol) to hydrogen molecules.

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Introduction

Nano/microporous carbons are a unique class of materials that are both safe and low in cost relative to many of their storage counterparts. The initial approach of this group involved an organically templated polymerization to produce microporous carbons. While pore size control was demonstrated, low surface areas lead to investigations involving micropore activation. Through these investigations, the activation of a high-temperature polymer, PEEK, was found to produce a promising microporous material. This activated PEEK had both high surface area (>3,000 m^2/g) and impressive hydrogen storage capabilities (>6 wt% at 2 bar).

Approach

Develop a simple, safe and cheap method for the preparation of doped and undoped micro/nanoporous carbon materials with high surface areas. Control the pore sizes and optimized H_2 binding energy. This is accomplished from the controlled oxidation of polymeric precursors under well controlled thermal and chemical conditions. More specific approaches include:

- 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.

Results

A porous carbon with high micropore content was achieved through the activation of PEEK. Figure 1a shows a transmission electron microscope (TEM) image demonstrating the microporosity of a sample of activated PEEK with an 82% burn-off and surface area of 3,103 m^2/g. TEM evidence also indicates the possibility of larger pores or voids in this high surface area sample; this is something that is common to PEEK activation trials and can be tuned via activation time. These pore/voids manifest themselves in H_2 NMR by a peak between 0-5 ppm. This can be seen in Figure 1b, which is the H_2 NMR of a sample with burn-off of 5% and surface area of 690 m^2/g. However, even at such low activation (burn-off) it is evident that micropores have developed to a significant extent as shown by the H_2 NMR peak at -5 ppm.

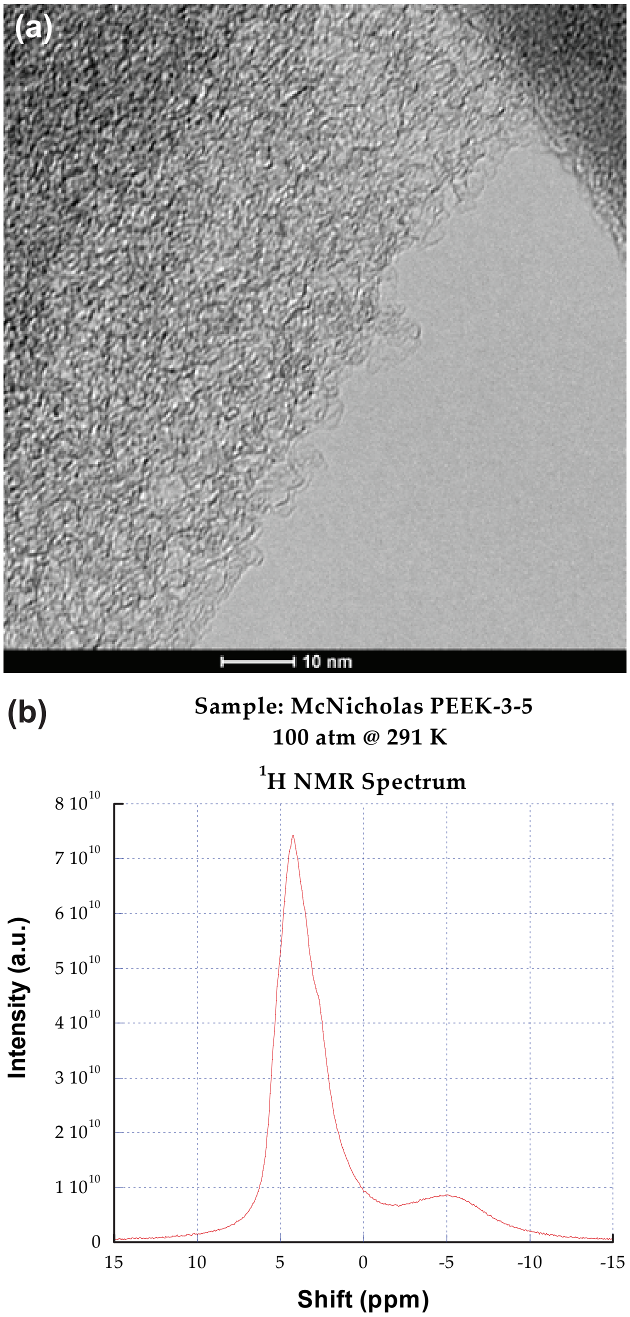

FIGURE 1. a) TEM Image of PEEK (Burn-Off 82% BET Surface Area 3,103 m^2/g); b) H_2 NMR of PEEK (Burn-Off 5% BET Surface Area 690 m^2/g)

Even more interesting than the high surface area and micropore content was the H_2 uptake data received from our collaborators at the National Renewable Energy Laboratory (NREL). Even the lowest activated

PEEK (burn-off 5%) demonstrated a H_2 uptake of 1.72 wt%, which with a surface area of 690 m^2/g correlates to a modified Chahine factor of 1.25. This factor indicates a higher H_2 uptake than predicted by simple surface interactions. This is supported by the binding energy, which was determined to be 8.5 kJ/mol (Figure 2a). This data indicated that this material may be very interesting for higher wt% storage. This was confirmed at the Annual Merit Review Meeting where our collaborators at NREL confirmed a H_2 sorption greater than 6 wt% for our most activated samples (82% burn-off). Another very interesting and promising property which arises from the H_2 NMR data is the qualitative comparison between spectra run at 120 K and room temperature (291 K). These spectra look very similar, indicating that H_2 is well absorbed even at room temperature, which is important for use in practical systems.

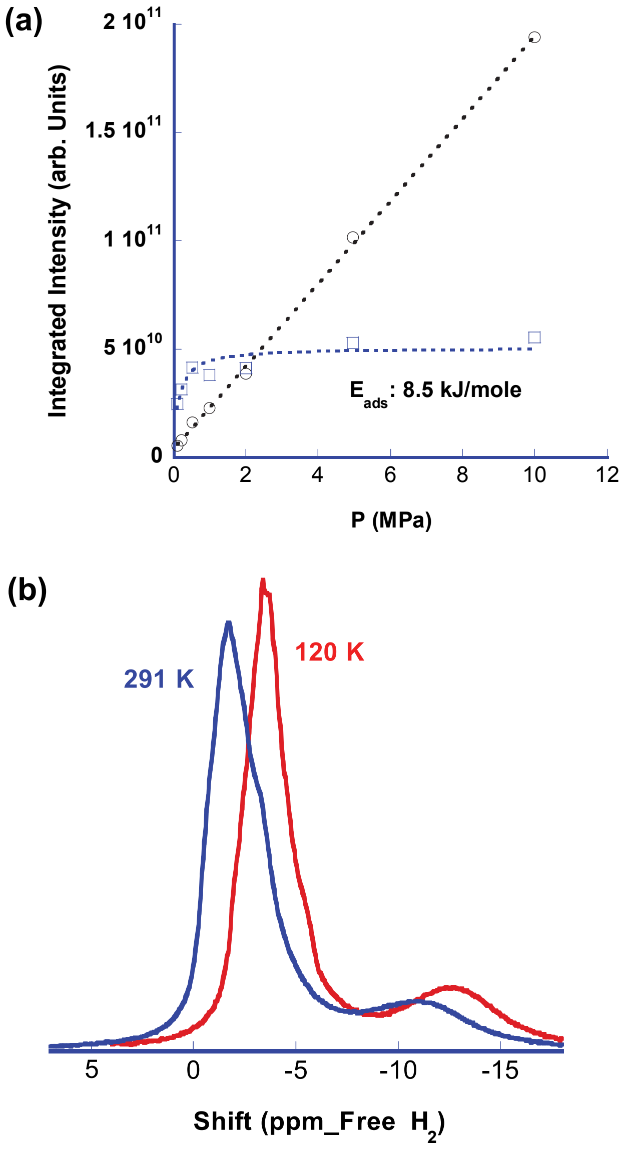

FIGURE 2. a) H_2 Absorption Energy Plot and b) H_2 NMR of PEEK (Burn-Off 5% BET Surface Area 690 m^2/g) at 120 K and Room Temperature (291 K)

Conclusions and Future Directions

By varying the activation time and temperature, pore diameter, surface area and thus binding energy can be tuned to produce a material which demonstrates great promise for H_2 storage. This group demonstrated a highly microporous carbon (pore diameter 1-3 nm) with very exciting surface area and H_2 binding energy (3,103 m^2/g and 8.5 kJ/mol, respectively). Future work will include:

- Steam activation of PEEK
- PEEK molding and activation
- Activation of additional high temperature polymers
- Contributions of material for spill-over studies for Dr. Yang (University of Michigan)

FY 2008 Publications/Presentations

1. "H_2 Storage in Microporous Carbons from PEEK Precursors", Thomas P. McNicholas, B.J. Anderson, Alfred Kleinhammes, Anmiao Wang, Yanqin Wang, Yue Wu, Jie Liu **(In Preparation, 2008).**

2. "Single-Walled and Few-Walled Carbon Nanotubes: From Synthesis to Applications", Staten Island College, City University of New York, May 1, 2008.

3. "Few Walled Carbon Nanotubes: Cheaper and Better Alternation for Single Walled Carbon Nanotubes in Bulk Applications", Fitzpatrick Institute for Photonics, Duke University, Dec. 4, 2007, Durham, NC.

4. "Few Walled Carbon Nanotubes: Cheaper and Better Alternation for Single Walled Carbon Nanotubes in Bulk Applications", The 6th Chinese Conference for Advanced Functional Materials (CCAFM), Nov. 18, 2007, Wuhan, China.

5. "Carbon Nanotubes: From Synthesis to Applications", Department of Chemistry, Nankai University, Nov. 19, 2007, Tianjin, China.

6. "Carbon Nanotubes: From Synthesis to Applications", Department of Chemistry, Tianjin University of Science and Technology, Nov. 20, 2007, Tianjin, China.

7. "Few-walled carbon nanotubes for bulk applications", ACS 2007 Fall Meeting, August 19, 2007, Boston, MA.

References

1. Cansado, I.P.P.; Goncalves, F.A.M.M.; Carrott, P.J.M.; Carrott, M.M.L.; Letters to the Editor: Carbon, *45* (2007) **2445-2458.**