

IV.C.1h 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 2015 hydrogen storage targets. Specific efforts include:

- Pore size control
- Surface area increase
- Metal doping of microporous carbon materials
- B 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 microporous carbons with the appropriate binding energies to meet the DOE 2015 hydrogen storage targets of:

- Cost: \$4/kWh net
- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L

Table 1 shows progress towards meeting the technical targets set for this project.

TABLE 1. Progress Towards Meeting Technical Targets for Storage

Characteristic	Units	Revised 2015 DOE System Targets for H ₂ Storage	Duke 2009 Materials Status
	wt%	5.5 wt%	~6 wt% at 77 K, 7 MPa
Volumetric Capacity	g/L	40 g/L	42 g/L*
Binding Energy	kJ/mol	NA	8.1

NA - not applicable
 *assuming density = 0.7 g/ml

Accomplishments

- Developed simple methods that could produce inexpensive hydrogen storage materials with specific energy densities above the DOE 5.5 wt% system target.
- Obtained porous carbons with variable pore diameters (including micropores with diameter 1-3 nm) from the thermal treatment of Poly(ether ether ketone) (PEEK) under CO₂ and steam environments; this is important because porous carbons with a large numbers of micropores and high surface areas have been proposed to be best for H₂ storage.
- Obtained a series of samples with high surface area (>3,000 m²/g) and high microporosity (improved from previous materials with specific surface areas ≤250 m²/g).

- Developed materials that are predicted to have ~6 wt% at 100 K, 7 MPa (70 bar) which corresponds to a 42 g/l volumetric capacity. It should be noted that this is a material storage capacity and not a system storage capacity. The material storage capacity will likely need to be significantly higher than this value to achieve a system storage capacity of 5.5 wt% and 40 g/L.
- Complimentary H₂-nuclear magnetic resonance (NMR) measurements showed >6 wt% storage at 120 K and 10 MPa. These results suggest that materials with large surface areas and optimized small diameter pores may be able to meet DOE hydrogen storage targets at temperatures higher than 77 K, decreasing the cost, weight and volume of the system.
- Optimized pore size materials showed higher binding energy (8.1 kJ/mol) to hydrogen molecules.
- Developed methods for successfully doping this high surface area porous carbon with variable amounts of B and Pd; these are important for binding energy tuning and spillover studies, respectively.
- Produced materials to evaluate the ability of potassium hydroxide (KOH) to improve pore volumes while conserving pore diameters.



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 primary approach of this group over the past year involved the thermal treatment of a high temperature polymer, PEEK, under CO₂ and steam environments. It was found that these methods reliably produce promising porous material with uniform pore diameters tunable to below 1 nm. These porous carbons derived from PEEK had both high surface area (>3,000 m²/g) and impressive hydrogen storage capabilities (~6 wt% at 7 MPa).

Approach

- Develop a simple, safe and cheap method for the preparation of doped and undoped meso and microporous carbon materials with high surface areas.
- Control the pore sizes for optimized H₂ binding energy. This is accomplished from the controlled oxidation of polymeric precursors under well-controlled thermal and chemical conditions. More specific approaches include:
 - Utilize controlled oxidation to increase the number and volume of micropores while increasing surface area.

- Variably incorporate dopants into various porous carbon precursors for the preparation of B and Pd doped microporous carbon materials.

Results

A porous carbon with high surface area and tunable pore size was achieved by thermally treating PEEK under CO₂ and steam environments. The products of both treatments yielded porous materials consisting primarily of carbon, with very little oxygen content as indicated by X-ray photoelectron spectroscopy (XPS, Figure 1). In both cases, this was true even after

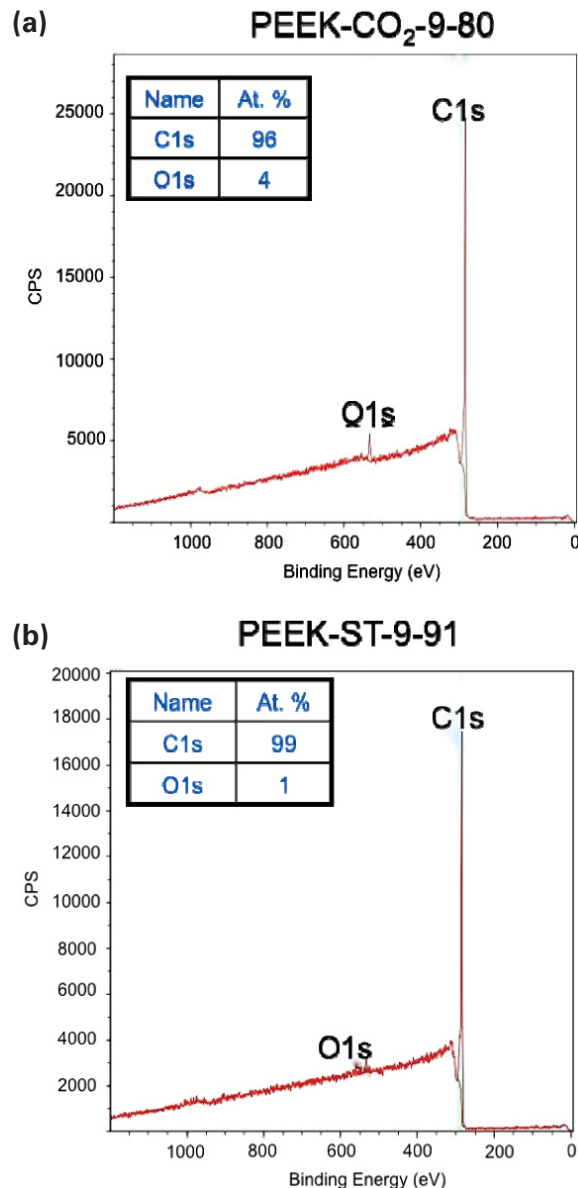


FIGURE 1. XPS of (a) PEEK-CO₂-9-80 and (b) PEEK-ST-9-91. Both spectra show that the porous carbon products derived from PEEK are nearly pure carbon materials.

extensive thermal treatment and thus at high surface areas; Figure 1 shows samples made using A) CO₂ and B) steam and having surface areas of 3,103 m²/g and 2,368 m²/g, respectively. This is an important aspect of these materials, as significant oxygen or other non-carbon content would change the H₂ binding energy and likely decrease the gravimetric density of the porous carbon products. Also, this fact is important for doping processes, as large oxygen contents would contribute to the formation of boron oxide and palladium oxide, both of which can interfere with their advantageous functions to H₂ sorption. As such, the H₂ sorption profiles of these pure carbon materials were investigated and compared to other pure and doped carbon materials both within and outside the DOE Hydrogen Sorption Center of Excellence in Table 2. It is evident that these materials are among the most promising and could be important in the future of H₂ storage applications. Gravimetric data of 3.7 wt% (26 g/l volumetric capacity) was demonstrated at 77 K and 2 bar (0.2 MPa); represents a 54% improvement over last year's maximum H₂ gravimetric uptake of ~2.4 wt%. Also of interest to these measurements was the fact that these large H₂ uptake values corresponded to large amounts of H₂ in pores as estimated by H₂-NMR from our partners at University of North Carolina (UNC). In many cases, more than 40% of the H₂ adsorbed resided in the pores. Furthermore, these materials have very high net capacities (~99% assuming a variable temperature fuel cell at 3 bar). This means that nearly all the H₂ stored in these products can be recovered and used as fuel. More detailed relative H₂ pore population measurements are presently being done by our partners at UNC.

In addition to the impressive H₂ sorption characteristics of these pure carbon materials, it was believed that they are very well suited for doping; B and Pd were investigated as specific areas of interest for doping because of their proposed binding energy enhancement and spillover capabilities, respectively. It is hoped that, by utilizing the enhancements of each dopant, a material can be produced in a scalable fashion that can be used to meet the DOE system targets. As such, two methods for producing doped porous carbon materials were designed. As can be seen in Figure 2A and 2C, variable amounts of B and Pd were successfully doped into our high surface area porous carbon. It is crucial that these doping procedures not introduce large amounts of oxygen to the resultant

TABLE 2. Porous carbon products derived from PEEK have large surface areas and impressive gravimetric and volumetric H₂ sorption data when compared to other pure and doped carbon materials. Materials in blue are produced using CO₂ whereas those in red are produced using steam. Other materials used for comparison are designated in maroon.

Material	BET SA (m ² /g)	H ₂ wt%	Volumetric Capacity (g/L)	% H ₂ in Micropores
PEEK-CO ₂ -9-1	524	1.6	11	45
B/C ¹	780	~1.6 (at 77 K 1.2 bar)		
PEEK-CO ₂ -9-5	700	2.0	14	
CMK-1 ²	1,788	2.19 (77 K, 1 bar)		
PEEK-CO ₂ -9-26	1,027	2.2	15	37
PEEK-ST-9-47	1,207	2.3	16	42
PEEK-ST-9-20	1,294	2.4	17	48
PEEK-ST-9-70	1,956	3.0	18	
AX-21 ³	3,300	~3.0 (77 K, 2 bar)		
PEEK-CO ₂ -9-80	3,103	3.7	26	28
Corncob ⁴	3,500	~5 (at 77 K, 20 bar)		

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 the National Renewable Energy Laboratory
4. Pfeifer, P.; RC 1 TT Presentation

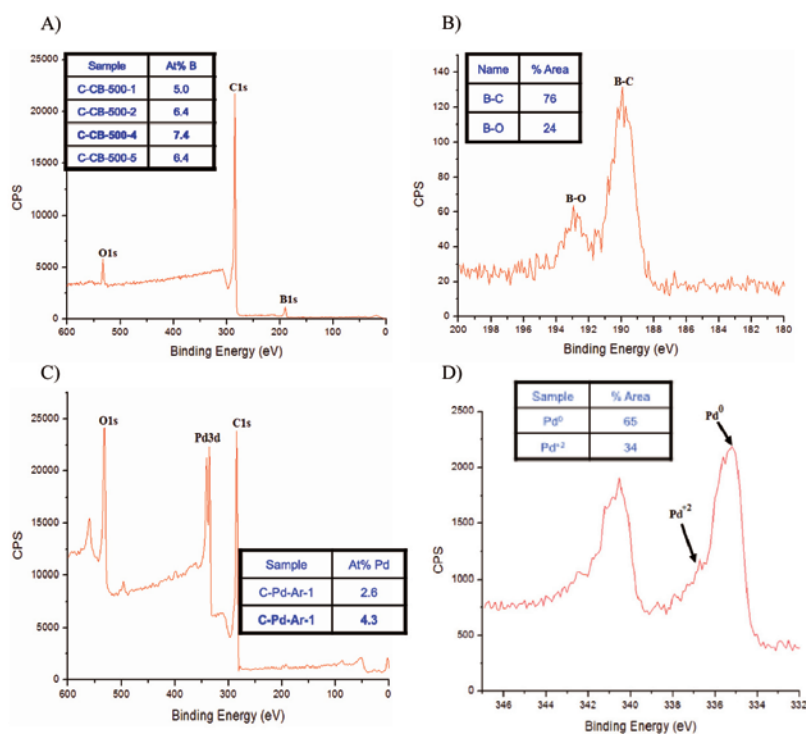


FIGURE 2. XPS data showing porous carbon materials doped with various amounts of B and Pd as displayed in A and C respectively. These spectra display that the products contain very little oxygen and consist primarily of dopant material and carbon. Spectra B and D respectively display that B and Pd exist in their elemental forms rather than as oxides. This is important for boron's enhancement of binding energy and for Pd's spillover characteristics to be realized.

materials, as was previously stated. Figure 2B and 2D demonstrate that the processes designed and utilized here produce products that are primarily oxide free. As such, tunable doping procedures which conserve surface area and porosity have been achieved herein. Our partners at the National Renewable Energy Laboratory and UNC are presently testing the H₂-binding energies and uptakes of these materials.

Conclusions and Future Directions

By varying the thermal treatment time and doping level, the pore diameter, surface area and thus binding energy can be tuned to produce materials which demonstrate great promise for H₂ storage. This group demonstrated a highly microporous carbon (pore diameter 1-3 nm) with very exciting surface area and H₂ binding energy (3,103 m²/g and 8.5 kJ/mol, respectively). Future work will include:

- Further high surface area B and Pd doped porous carbon production and analysis.
 - PEEK thin films.
- Further PEEK thermal trials at different temperatures.
 - Further contributions of material for spillover studies for Dr. Yang (University of Michigan) and H₂-NMR calibration at UNC.

FY 2009 Publications/Presentations

1. “H₂ 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, 2009).
2. “Single-Walled and Few-Walled Carbon Nanotubes: From Synthesis to Applications”, Staten Island College, City University of New York, May 1, 2008.

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