IV.C.3 Nanostructured Activated Carbon for Hydrogen Storage

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Objectives

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with at least 7 wt% materials-based gravimetric capacity and 50 g H_2/L materials-based volumetric capacity, with the potential to meet the DOE 2010 system-level targets.

- Prepare and characterize nanostructured polymer derivatives as carbon precursors.
- Initiate the production of nanostructured activated carbon for hydrogen storage.
- Develop methods for sorbent-based doped polymer/carbon.

Technical Barriers

This project addresses the following On-Board Hydrogen Storage Technical Barriers section 3.3.4 outlined in the Hydrogen, Fuel Cells and Infrastructure Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rate

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

Research and development on novel high surface area nanostructured carbons for hydrogen storage is being conducted in this project. The project aims to address the critical need that has been recognized by the DOE, which has established a national effort to develop new and advanced high-capacity hydrogen storage materials and technologies. This project focuses on the synthesis of inexpensive carbon-based high surface area sorbents that can combine hydrogen via moderate physical and chemical interaction forces. These new materials and concepts have been designed to meet the DOE 2010 goals concerning the production of low-cost, high specific energy and energy density hydrogen storage materials (Table 1).

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	FY 2007-2008 Materials **
Specific Energy	kWh/kg (wt% H_2)	2.0 (6 wt%)	2.4 (7 wt%)
Volumetric Energy Capacity	kWh/L	1.5	1.2 – 1.5
Desorption Temperature	K	233–358	77
Plateau Pressure	bar		60

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

Project Milestone Completed

- Synthesis of at least five materials and demonstration of reproducible measurement of storage capacity.
- Down-selection of optimum materials, demonstration of a set of materials with reversible storage capacity of ~7 wt% and ~33 g H_2/L.

Accomplishments

- Screened and down-selected synthesis conditions for carbon nanostructure.
- Developed novel activation systems for synthesis of high surface area nanostructured polymer carbons (~4,000 m^2/g).

- Down-selected carbon nanostructures with demonstrated material-based hydrogen storage capacity of ~7.3 wt% (33 g H_2/L), and ~5.8 wt% (~46 g H_2/L) at 77 K and 6 MPa.
- Achieved production reproducibility >98% in terms of surface area and average pore diameter in scale-up synthesis (10 g/batch) of modified PEEK carbon.
- Doped high surface area carbon with multicyclic ligand compounds $[CNH]_n^+F_n^-$.

✧   ✧   ✧   ✧   ✧

Introduction

The State University of New York - Polymer Research Institute in Syracuse has initiated a collaborative effort to develop superior high surface area nanostructured carbon for hydrogen storage. The precursor for the synthesis of the polymer-carbon has been developed from a series of nanoporous semicrystalline oriented polymers having nanosize pores, with uniform pore size distribution and high surface area. The precursor is tailored to form activated carbon with slit-like microporous structure (pore width ~7-20 Å) and high surface area (S_{BET} >3,000 m^2/g). The high surface area of the polymer precursors enables doping initial material with chemical agents, which upon carbonization, introduces specific interaction sites that significantly increase the hydrogen storage capacity of the nanostructured carbon material.

Approach

Nanostructured polymer-carbons were synthesized by tailoring the morphology of the polymer precursors as to produce carbon with the proper morphology for activation to afford high surface area and controlled micropores. Thus, procedures were developed to carbonize certain polymers like MPEEKs. At this stage parameters such as heating rate, temperature and exposure period were studied. At the second stage the pore creation by an activation step, the activation kinetics, including reactivity, size of activation agents, and the homogeneity of the activation system, has been addressed to control the polymer-carbon texture.

- Processing the precursors (modified poly(phenylene oxide), MPEEK, and poly(etherimide)) at high melt shear rates further controls the morphology and orientation of crystalline regions.
- **Hydrogen Storage (Physisorption and Chemisorption).** Prepare carbon and activated polymer – based carbons, determine the storage characteristic, surface area, pore size distribution, and micropore volume prepared with various activation agents.

- **Physisorption in Carbon/Polymer.** Conduct H_2, N_2 and He adsorption measurements. Study and correlate surface area, micropore volume, pore size distribution and storage to the methods of the carbon synthesis.
- **Chemisorption.** Study methods of incorporating reactive sites into the pores of active carbon/polymer. Investigate organo-metallics and metal hydrides and multicyclic ligands-doped carbons.

Results

In Fiscal Years 2007-2008, more than 100 batches of polymer-based nanostructured carbons were synthesized and screened. Figure 1 illustrates the impact of the pore evolution process on the surface area, S_{BET}, and average pore diameter, d_{DR}, during activation. Two opposite trends were observed: S_{BET} increasing while d_{DR} decreasing (micropore formation), and S_{BET} and d_{DR} simultaneously increasing (pore enlargement). Competition between these two processes dictates the porous texture of the final material. The targeted porous texture requires S_{BET} >2,600 m^2/g and d_{DR} ~8 Å. The current activation process produces carbons of various porous textures. At one end are those with the preferred pore size (d_{DR} ~8 Å) but modest surface area (S_{BET} ~1,300 m^2/g), and at the other end those with the desired high surface area (S_{BET} ~4,000 m^2/g) but enlarged pore size (d_{DR} ~ 21 Å). Consequently,
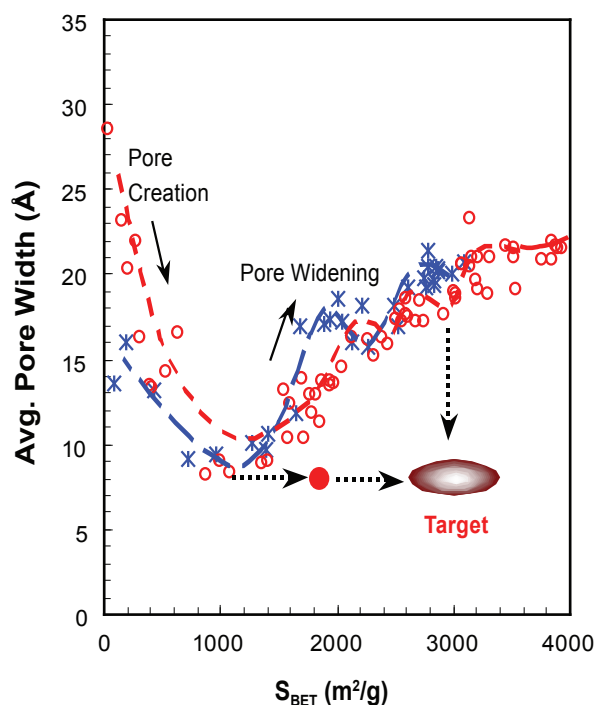

FIGURE 1. Correlation of Surface Area with Pore Size of Activated Polymer Carbons

a secondary pore formation process was introduced to post modify the pore structure, by scaffolding high surface area carbon with multicyclic compounds like $[CNH]_n$ (Figure 2), which yielded a material with increased S_{BET} ~1,800 m^2/g yet retained a small pore size, d_{DR} ~8 Å.

Table 2 summarizes the porous texture of down-selected high surface area carbon nanostructures. Hydrogen uptake of these carbon nanostructured materials has been measured by independent laboratories (including two national laboratories), and is shown in Figure 3. At 77 K and hydrogen pressure of 5 MPa, hydrogen gravimetric storage capacity, $W(H_2)$ up to 7.3 wt% has been achieved by APKI6SN4. On the basis of carbon apparent density, this material gives a volumetric storage capacity, $V(H_2)$ ~32 g H$_2$/L. The highest volumetric capacity, $V(H_2)$ ~46 g H$_2$/L, is achieved by MK725.

While at 77 K and modest pressure the performance of the polymer carbons approaches and even surpasses the target storage capacity values, they are falling short of room temperature application. At 298 K and 6 MPa, gravimetric storage capacity less than 1 wt% is accomplished. The low storage capacity at room temperature is due to the weak hydrogen binding energy, currently E_{ad} ~ –6 kJ/mol (up to –7.8 kJ/mol at <1 bar) (Table 2), for all carbons shown here. Increasing hydrogen binding energy, by introducing a large number of interacting and ionic sites that are attached on a polymer framework to the polymer carbons, is currently underway.

The maximum excess hydrogen uptake of these carbon nanostructures exhibit a linear dependence on Brunauer-Emmett-Teller (BET) surface area (Figure 4), with a slope value corresponding to ~20 µg H$_2$/(m^2/g),
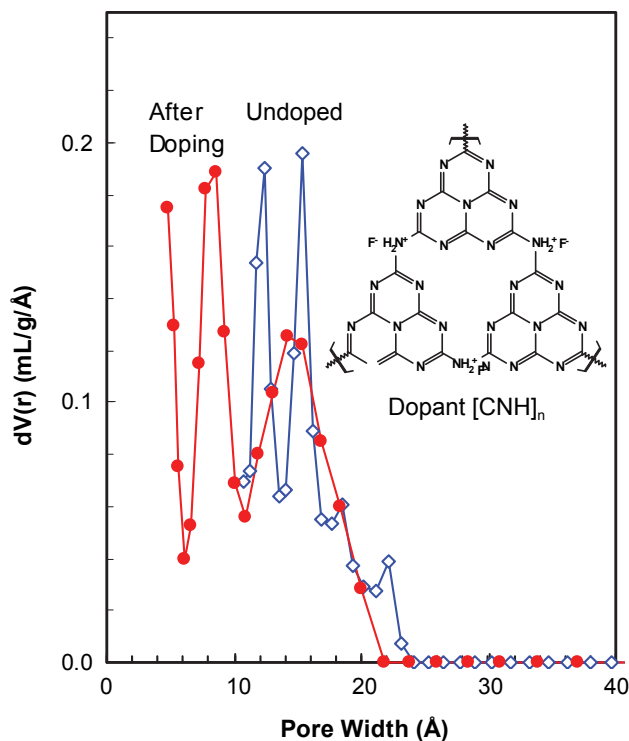

FIGURE 2. Impact of $[CNH]_n$ Doping on Pore Size Distribution

TABLE 2. Porous Texture and Hydrogen Storage Capacity of Polymer-Based Activated Carbon

Sample	S_{BET} m^2/g	V_{pore} mL/g	V_{mp} mL/g	d_{DR} Å	ρ_a g/mL	W(H$_2$), wt%		V(H$_2$), g H$_2$/L		E_{ad} ** kJ/mol
						77 K, 60 bar	298 K, 60 bar	77 K, 60 bar	298 K, 60 bar	
MK725	1,800	0.87	0.84	14.6	0.749	5.8	0.80	46.1	6.4	-5.9
PKMNa	1,765	0.74	0.72	12.9	0.828	4.5	0.47	38.7	3.9	-
MK750P	2,440	1.07	1.00	15.8	0.651	4.9	0.41	33.2	2.7	-
APK6S11	2,480	1.20	1.14	17.6	0.601	5.3	0.40	33.6	2.5	-6.3
PKMK_Bulk	2,490	1.08	1.08	18.6	0.648	5.1	0.59	35.1	3.8	-
APOR8	2,550	1.26	1.15	19.4	0.580	6.0	0.50	37.3	2.9	
PK775C	2,680	1.15	1.10	18.5	0.619	5.6*	N/A	36.7*	N/A	-
APKIS13	3,025	1.38	1.29	18.8	0.542	5.9	0.48	33.8	2.6	-
APKI6S7	3,320	1.67	1.49	19.1	0.468	6.3	0.50	31.5	2.5	-5.8
APKI6SN3	3,300	1.85	1.47	18.8	0.432	6.5	0.45	30.0	2.1	-5.6
APO-R10	3,890	2.20	1.72	22.1	0.375	6.4	0.50	25.7	2.0	-5.7
APKI6SN5	4,020	2.30	1.75	20.6	0.440	6.7	0.59	31.6	2.8	-5.7
APKI6SN4	3,900	2.30	1.70	21.6	0.407	7.3	0.50	32.5	2.0	-

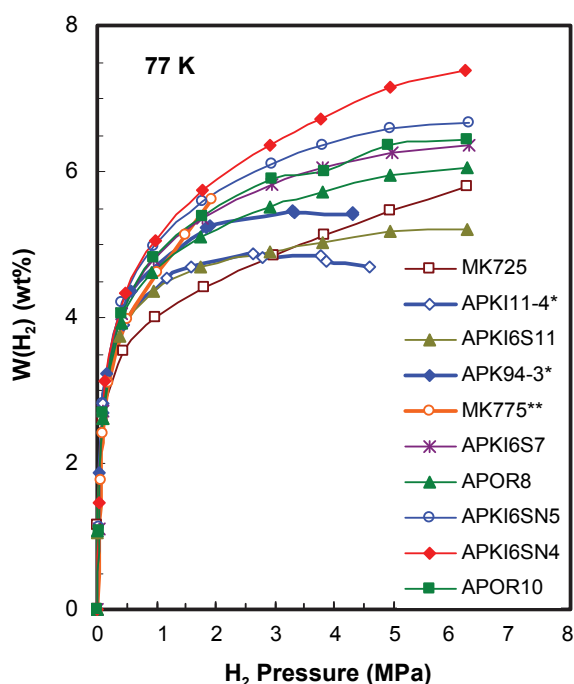* Measured at 77 K and 20 bar. ** Determined by Clausius-Clapeyron Equation at 1 wt% hydrogen uptake

FIGURE 3. Excessive Hydrogen Uptake of Polymer Carbons at 77 K and High Pressure
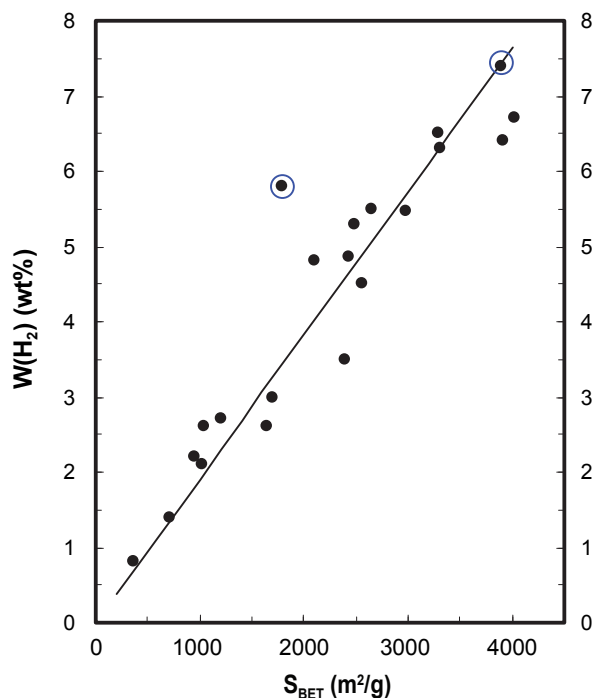

FIGURE 4. Dependence of Maximum Excessive Hydrogen Uptake at 77 K on BET Surface Area

which approaches the saturated monolayer coverage of hydrogen molecules on a carbon surface.

The robustness of the currently developed synthetic method to these unique high surface area activated MPEEK carbons is demonstrated by the superior reproducibility in batch production (Table 3).

TABLE 3. Reproducibility of the Production of Activated Polymer Carbons

Batch	S_{BET} m^2/g	d_{DR} Å	V_{mp} mL/g	V_{pore} mL/g	ρ_a g/mL
1	3,880	21.6	1.69	2.22	0.372
2	3,960	21.0	1.75	2.22	0.372
3	3,890	21.6	1.70	2.23	0.371
4	3,875	21.6	1.68	2.22	0.371
5	3,760	20.7	1.67	2.17	0.375
6	4,070	21.7	1.76	2.47	0.369
7	3,880	21.5	1.66	2.36	0.372
8	3,810	21.4	1.65	2.47	0.369
Avg	3,890 ±90	21.4 ±0.4	1.70 ±0.04	2.30 ±0.11	0.371 ±0.001

Conclusions and Future Directions

The highlights of the present study are:

- Demonstrated synthesis of carbons with high surface area (up to 4,000 m^2/g) and low average pore width (down to 8.5 Å).
- Accomplished gravimetric storage capacity of ~7 wt%, and volumetric capacity of ~46 g/L at 77 K.
- Formulated synthetic strategies toward polymer-based nanostructured carbons of controllable porosity and surface area.
- Achieved reproducibility (>98% in terms of surface area and pore volume) in 10-gram batch production of high surface area carbon.

The present effort aims toward increasing hydrogen binding energy to the polymer-carbon by surface modification and doping with heterocyclic and heteroaromatic polymers and organo-metallics. In this regard, carbon doping with organo-metallic compounds that exhibit rigid planar configuration and are rich in electronegative nitrogen atoms, $[CNH]_n$, may enable the DOE targeted temperature and moderate pressure H_2 storage system. We will continue to develop, modify, characterize and scale-up production of nanoporous polymer materials and carbons to establish correlation between chemisorption of hydrogen with surface area, pore size and porosity.

FY 2008 Publications/Presentations

1. Y. Yuan; I. Cabasso; and H. Liu, "Surface Morphology of Nanostructured Polymer-based Activated Carbons", *J. Physical Chem. B*, 2008 July on Web.

2. Q. Nan; Y. Yuan; X. Wang; and I. Cabasso, "Polymer-based activated carbon for hydrogen storage", *212th Electrochemical Society Meeting*, Poster, Oct. 7–12, 2007, Washington, D.C.

3. Four DOE Quarterly Reports for FY 2008.

4. I. Cabasso; Xinwei Wang; and Youxin Yuan, "Polymer-based activated carbon for hydrogen storage", *DOE Annual Merit Review Highlights Hydrogen and Fuel Cell Projects*, Poster, June 9-13, 2008, Crystal City, VA.