

IV.C.3 Nanostructured Activated Carbon for Hydrogen Storage

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Contract Number: DE-FG36-05GO15009

Subcontractor:

PoroGen, LLC, Boston, MA

Start Date: May 2, 2005

Projected End Date: April 30, 2009

- (E) Refueling Time
- (M) Hydrogen Capacity and Reversibility
- (N) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

R&D on novel, high surface area nanostructured carbons for hydrogen storage is 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 is focused on the synthesis of inexpensive carbon-based high surface area sorbents that can be combined with chemical-interacting organic, and/or inorganic materials. These new materials and concepts have been designed to meet the DOE's 2010 goals concerning the production of low-cost, high specific energy and energy density hydrogen storage materials.

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2007 System Target	2010 System Target
Specific Energy	kWh/kg (wt.% H ₂)	1.5 (4.5 wt.%)	2.0 (6 wt.%)
Volumetric Energy Capacity	kWh/L (kg H ₂ /L)	1.2 (0.036)	1.5 (0.045)

Objectives

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with at least 7 wt% materials-based gravimetric capacity and 50 g H₂/L materials-based volumetric capacity, with the potential to meet the DOE 2010 system-level targets.

- Prepare and characterize nanostructure poly(ether ether ketone) (PEEK) derivatives.
- Initiate the production of nanostructure activated carbon.
- Develop methods for organometallic-doped PEEK/carbon.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) outlined in the Hydrogen, Fuel Cells and Infrastructure Multi-Year Research Development and Demonstration Plan:

- (A) Cost
- (B) Weight and Volume
- (C) Efficiency
- (D) Durability

Accomplishments

- Comprehensive 3-D correlations of surface area and average pore diameter versus volumetric and gravimetric hydrogen storage capacity (at 77 K, 1 bar) have been established.
- Novel activation agents (N/K* and K*/M) have been developed for synthesis of high surface area PEEK carbon with exceedingly narrow pore size distributions (ultramicroporosity, up to 78%).
- Materials-based hydrogen storage capacity of ~2.9 wt.% [$\sim 27 \text{ g H}_2/\text{L}_{(\text{carbon})}$] at 77 K (1 bar).
- Reversibility of hydrogen storage capacity, > 99%, has been demonstrated in multiple cycle runs (10-20 cycles) for randomly selected samples.
- High reproducibility ($\pm 3\%$) in batch synthesis of nanostructured PEEK carbons has been achieved.
- A new approach has been developed for uniformly doping PEEK carbons with metal nanoparticles.

Introduction

The State University of New York (Syracuse esf) and PoroGen, LLC, have initiated a collaborative effort to develop superior high surface area nanostructured carbons for hydrogen storage. The synthesis of the carbon starts with the preparation of a nanoporous semicrystalline oriented polymer precursor having nanosize pores, with uniform pore size distribution and high surface area. The semicrystalline nanoporous polymer material is tailored to form activated carbons with slit-like microporous structure and high surface area (pore width $\sim 0.7\text{-}2.0$ nm). The high surface area of the polymeric precursor aids in preparation of this unique carbon ($S_{\text{BET}} > 3,000$ m²/g) and enables doping initial material with chemical agents that upon carbonization, introduces specific interaction sites that significantly increase the hydrogen storage capacity of the nanostructured carbon material.

Approach

Carbonization processes are being performed on a blend of poly(ether ether ketone) (PEEK)/polyetherimide (PEI) precursor that is spun at high melt shear rates. Highly oriented lamellae crystals are formed in the nanoporous polymer material by extruding the PEEK/PEI blend at high draw ratios while controlling the morphology and orientation of crystalline regions. High orientation of polymer chains and the alignment of crystalline lamellae regions lead to formation of a porous material with oriented nanosize pores that upon carbonization, with specific activation agents, produce activated carbon with angstrom-size slit-like pores (Figure 1).

Reactive sites can be incorporated into the pores of active carbon/PEEK to promote a significant increase in hydrogen adsorption. The incorporation of organometallics and metal oxide-doped carbon into catalytic sites containing heteroatoms, such as N, P, S and B, are being investigated. Large quantities of materials can and have been synthesized on a laboratory scale.

Results

Various types of PEEK blend precursors have been synthesized to produce high carbon yields with the proper morphology for activation to afford high surface area and controlled angstrom-size pores. In this segment of the research, the rate of heating, carbonization and activation catalysts were identified and studied. In order to control the activated carbon texture, and to eliminate the possibility of producing mesopores and macropores, the kinetics of the activations was studied aiming toward homogeneity of the activating catalyst in the carbon

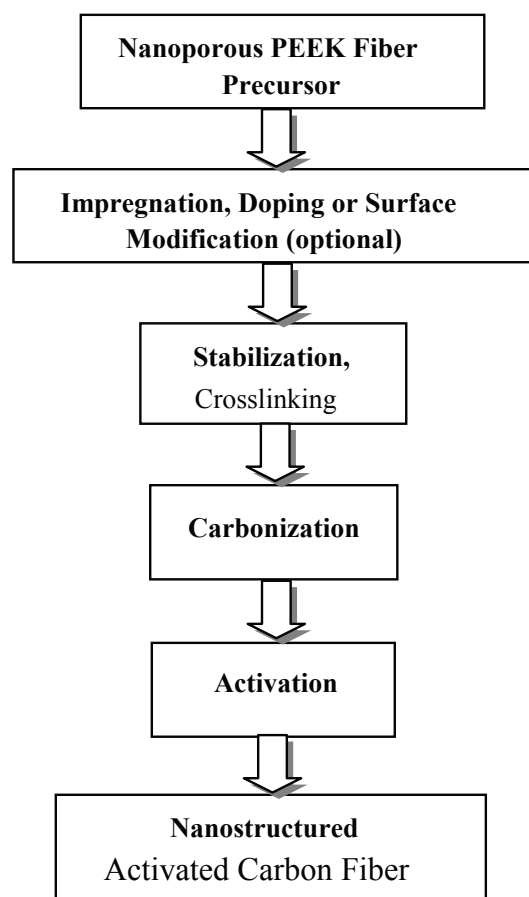


FIGURE 1. Processing of Nanoporous PEEK Carbon Materials

matrix. The latter was attained by the development of a set of new catalysts designated N* and N/K*.

Figure 2 illustrates the pore size distribution of nanostructured PEEK carbons activated by K⁺, N* and N/K* catalysts. Activation with N* and N/K* leads to an exceptionally narrow pore size distribution, with a majority of pores having a pore diameter of ≤ 10 Å.

Specific surface area, ultramicropore volume (pore diameter ≤ 7 Å), hydrogen binding energy, average pore diameter and hydrogen storage capacity of various activated PEEK carbons are listed in Table 2. A gravimetric capacity of up to ~ 2.9 wt% and volumetric capacity of up to 27 g H₂/L_(carbon) (at 77 K, 1 bar) have been obtained. Hydrogen binding energy on these carbons are $\sim -6.4\text{-}6.85$ kJ/mol, which fall in the same range of typical carbon materials. The density of hydrogen in micropores ranges from 0.02–0.05 g/mL, which is lower than that of liquid hydrogen (0.07 g/mL at 33 K, 1 bar); a substantial increase of hydrogen adsorption capacity has been recorded at high pressure.

The correlation of the material-based gravimetric and volumetric storage capacity (77 K, 1 bar) with surface area and average pore size is presented in

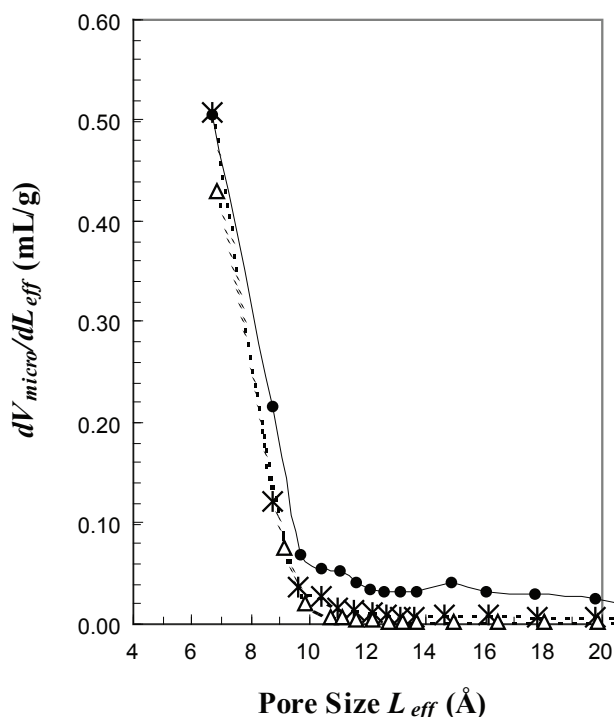


FIGURE 2. Harvath-Kawazoe pore size distribution of PEEK carbons activated by (●) C/K* (mol.) = 1/0.73, (*) C/N (mol.) = 1/1, and (△) C/N/K* (mol.) = 1/1/0.1.

Figure 3 which combines experimental data collected from 50 carbons. The 3-D plot shows that, initially, the gravimetric capacity [W_{H_2}] increases rapidly with surface area [S_{BET}] up to ~ 2000 m^2/g , the progression slows down with the further augmentation in S_{BET} . In contrast, volumetric capacity [V_{H_2}] exhibits a maximum at surface area range of 1400-1900 m^2/g . Decrease in the pore diameter leads to higher W_{H_2} and V_{H_2} , thus, for a set of carbons with the same S_{BET} , but different average pore diameter [d_{DR}], higher W_{H_2} and V_{H_2} are found

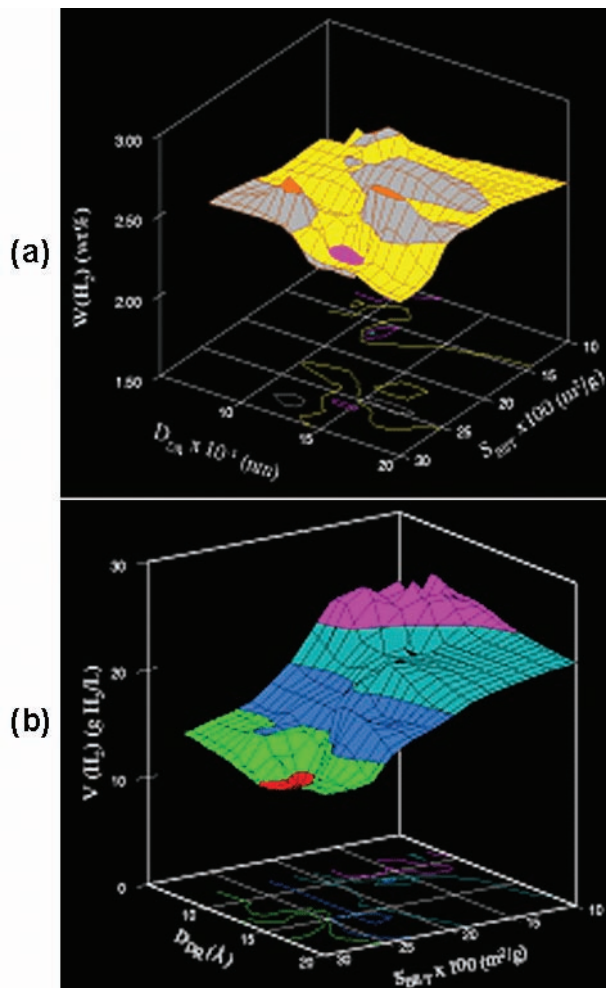


FIGURE 3. 3-D plot of (a) gravimetric and (b) volumetric hydrogen storage capacity (77 K, 1 bar) dependence on surface area and average pore size.

TABLE 2. Characterization of Activated PEEK Carbons

Activation Condition ^a	W (H ₂) (wt.%)	V(H ₂) ^b (g/L)	ρ_{adH_2} (g/mL)	S_{BET} (m ² /g)	V_{ultra} (mL/g)	-E _{ad} (kJ/mol)	V_{ultra}/V_{micro} (%)	ρ_a (g/mL)	d_{DR} (Å)
C/K* (1/0.73)	2.45 ± 0.03	14.9 ± 0.3	0.023	2870	0.47	6.45 ± 0.06	38.8	0.595	26.70
C/N (1/1)	2.74 ± 0.02	22.6 ± 0.3	0.036	1650	0.51	6.69 ± 0.06	65.4	0.803	14.01
C/N/K* (1/1/0.10)	2.64 ± 0.02	27.2 ± 0.3	0.048	1430	0.44	6.80 ± 0.08	77.2	1.000	9.92
C/KM (1/0.8)	2.56 ± 0.02	25.9 ± 0.3	0.048	1410	0.44	6.84 ± 0.08	76.3	0.960	9.10
C/KM (1/1.2), 700°C	2.64 ± 0.03	22.2 ± 0.2	0.037	1850	0.53	6.51 ± 0.06	64.0	0.812	11.30
C/KM (1/1.2), 725°C	2.91 ± 0.03	22.5 ± 0.2	0.036	2040	0.53	6.61 ± 0.07	60.7	0.748	14.60
C/KM (1/1.2), 775°C	2.91 ± 0.02	18.5 ± 0.4	0.027	2680	0.58	6.45 ± 0.06	50.4	0.618	17.20
C/KM (1/1.2), 850°C	2.81 ± 0.03	14.6 ± 0.3	0.022	3135	0.57	6.41 ± 0.05	40.3	0.503	20.40

^a Activation temperature 700 °C.

^b Assuming that the bulk packing density is equivalent to the apparent carbon density ρ_c .

TABLE 3. Reproducibility of Synthesis of High Surface Area PEEK Carbons

Batches*	S _{BET} (m ² /g)	V _{ultra} (mL/g)	V _{micro} (mL/g)	V _{pore} (mL/g)	V _{micro} / V _{pore} (%)	d _{DR} (Å)
1 st	2820	0.589	1.189	1.263	94.1	18.2
2 nd	3135	0.558	1.320	1.549	85.2	20.6
3 rd	2985	0.566	1.279	1.359	94.1	18.6
4 th	2820	0.589	1.178	1.260	93.5	18.2
5 th	2865	0.550	1.029	1.167	88.2	19.0
6 th	2940	0.582	1.252	1.327	94.3	18.6
7 th	2740	0.556	1.149	1.230	93.4	18.3
Avg.	2900	0.570	1.199	1.308	91.9	18.8
R ²	0.955	0.972	0.920	0.906	0.963	0.955

*Produced at same carbonization and activation condition.

for the smaller d_{DR}. As shown in Figure 3a and 3b, a nanostructured activated carbon with a high surface area (S_{BET} ~2500-3000 m²/g) and narrow pore size (d_{DR}, ~10 Å) and high ultramicropore volume (~0.5–0.6 mL/g) registers the highest gravimetric hydrogen storage capacity (2.9±0.02 wt%) at 77 K and 1 bar. In contrast (Figure 3b), the highest volumetric storage capacity (up to 27.2±0.3 g H₂/L carbon at 77 K, 1 bar) has been recorded for carbons within region of: S_{BET} ~1400-1600 m²/g and d_{DR} ~10 Å, and having highest ultramicropore volume porosity (~78%). This phenomenon is due to carbon having different ultramicropore volume and porosity. The ability to decrease the pore size while increasing S_{BET}, ultramicropore volume and porosity is critical in order to achieve both high W_{H2} and V_{H2}. Note however, this is the case for the low pressure adsorptions; above 1 bar the V_{H2} is pressure dependent and the system shifts its course. Data are still being collected to account for high pressure systems.

The synthetic method that has been developed in this project successfully yielded high surface area activated carbon that is highly reproducible, as is demonstrated by the batch production (Table 3).

Moreover, these activated carbons demonstrate full recover-ability in its storage capacity after being subjected to multi-cycle (5-10 cycles) hydrogen uptake tests (77 K, up to 1 bar), suggesting that the carbon pore structure remains intact. Between cycles, carbon was fully desorbed at 200°C after at least 30 min.

During this reporting period, we also developed a new approach to dope metallic nanoparticles (presently nickel) into the carbon matrix. A series of carbons doped with 0.9-19.5 wt.% of nickel nanoparticles have been synthesized. Their back-scattering scanning electron microscope (SEM) images are depicted in

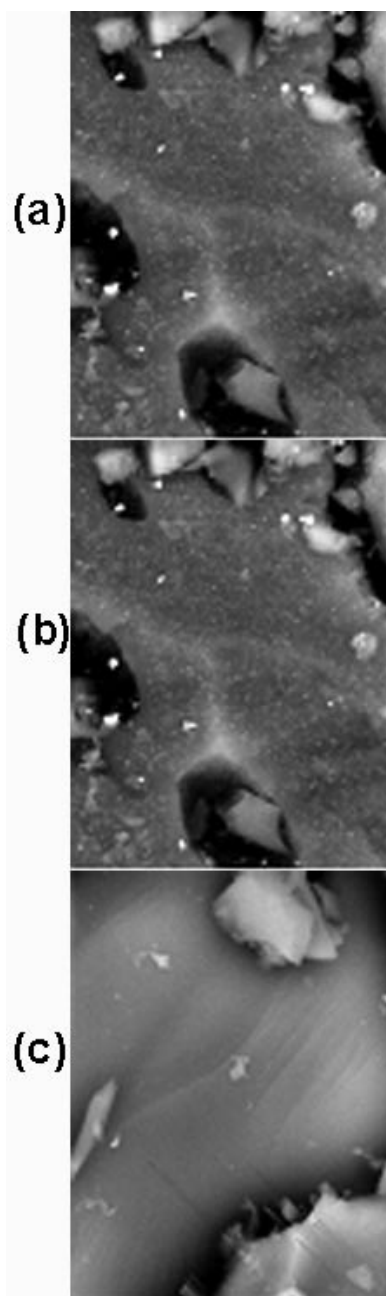


FIGURE 4. Back-scattering SEM micrographs of: 20 wt.% metal-doped (a), 5 wt.% metal-doped (b), and non-doped (c) PEEK carbons (all samples are of pre-activated carbon).

Figure 4. At a modest doping level of 4.6-19.5 wt.%, nickel was uniformly dispersed in the carbon matrix. The diameter of nickel particles reduces from 160 ± 30 nm to 100 ± 35 nm as the doping level drops from ~19.5 to ~4.6 wt.%; at ≤1.4 wt.% doping, nickel particles appear to be too small to be observed by SEM. X-ray diffraction study reveals the presence of face-centered nickel crystals at a doping level of ~4.6-19.5 wt.%. Reduction of the nickel particle size to 10-40 Å is one of the aims of this part of the project.

Conclusion and Future Direction

- The synthesis segment of this work proved that nanostructured PEEK carbons could be produced successfully by applying novel catalysts and synthetic procedures. The products can be tailored to have: elevated surface areas, controlled pore size distribution and diameter, high ultramicropore volume ($V_{\text{ultra}} \sim 0.58 \text{ mL/g}$) and high ultramicroporosity. The nanostructured carbons exhibit progressively higher hydrogen storage capacity, as the synthesis is fine-tuned. Presently, only 50-60% of the pore volume is fully occupied indicating that the performance of the carbons can be considerably higher.
- Continue to develop, modify, characterize and verify nanostructured porous carbons for hydrogen storage. The primary direction forward

is to increase the fraction of ultramicropores and narrowing the pore size distribution to $\sim 0.5\text{-}0.8 \text{ nm}$. Test the H_2 adsorptions at high pressure 1-100 bar.

- Continue development of the metal (nickel) doped carbon at the 1-2 nm range.
- Continue to develop methods of carbon doping with metal hydrides (MH_n , RSiH_n), transitional metals (Ti, Ni, V) and organometallic compounds, in addition to the tests of hydrogen adsorption at elevated temperatures.

FY 2006 Publications and Presentations

1. A poster was presented at the DOE Annual Merit Review Meeting in Washington, D.C. (May 2006).