

IV.C.8 Nanostructured Activated Carbon for Hydrogen Storage

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Subcontractor:

PoroGen, LLC, Boston, MA

Start Date: May 2, 2005

Projected End Date: June 30, 2010 (no-cost
extension to December 31, 2011)

Fiscal Year (FY) 2011 Objectives

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage material which has at least a 5.5 wt% materials-based gravimetric capacity and a 40 gH₂/L material-based volumetric capacity at 235–358 K, and potential to meet the DOE 2015 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 (2007) section 3.3.4 outlined in the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(C) Efficiency

(E) Charging/Discharging Rate

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

The research and development of novel high surface area nanostructured carbons for hydrogen storage has been conducted in this project. The project aims to address the critical need that has been recognized by DOE, which has established a national effort to develop new and advanced high-capacity hydrogen storage materials and technologies. This project is applied toward the synthesis of inexpensive carbon-based, high surface area sorbents that can be combined with chemical-interacting organic, and/or inorganic materials, to yield high storage materials. These new materials and concepts have been designed to meet the DOE 2015 goals concerning the production of low-cost, high specific hydrogen binding energy hydrogen storage materials.

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2015 System Target	SUNY-Syracuse**
System Gravimetric Capacity	kWh/kg (wt% H ₂)	1.8 (5.5 wt%)	2.4 (7.2 wt%)
System Volumetric Capacity	kWh/L (gH ₂ /L system)	1.3 (40)	1.2 (40)
Min/Max Delivery Temperature	K	233–358	77
Max Delivery Pressure	bar	100	60

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

FY 2011 Accomplishments

- New type of polymer-based carbons that incorporate the metal (or metal ion) with high surface area and narrow pore size distribution has been developed with a hydrogen storage capacity of ~3.0 at 77K, 1 bar.
- Demonstrate the synthesis of modified polymer-based carbons with high surface area and low average pore width. Accomplished gravimetric storage capacity of ~6.7-7.0 wt% (77 K, 60 bar) and volumetric capacity 8 g H₂/L (237 K, 60 bar) with a high reproducibility on production in laboratory scale!
- Detail study on composition and morphology of new type of carbon nanotube with Fe and other metal into organocyclic-CN_n macromolecules rich with unsaturated bonds that should be available for room

temperature (RT) application at moderate pressures for H₂ storage systems.

- Products with an unlimited self-life! (Stable to extreme weather condition, including high humidity and temperature variation.)
- Products perform well at relatively low pressure (<20 bar).



Introduction

The State University of New York (esf) and PoroGen, LLC, have initiated a collaborative effort to develop superior high surface area nanostructured carbons for hydrogen storage. Synthesis of the carbon starts with the preparation of a nanoporous semicrystalline oriented polymer precursor having nanosize pores, with a uniform pore size distribution. This semicrystalline nanoporous polymer precursor is subsequently tailored to form high surface area activated carbons with slit-like microporous structure (pore width ~7-20 Å). The high surface area of the polymeric precursor aids in preparation of this unique carbon (Brunauer-Emmett-Teller surface area, $S_{\text{BET}} > 3,000 \text{ m}^2/\text{g}$) and 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

To achieve the project objectives, polymer-based nanostructured carbons have been synthesized by engineering the structure of the polymer precursors to produce carbon with the designed morphology for activation to high surface area and controlled micropores. Thus, polymer precursors (modified poly(phenylene oxide), MPEEK, poly(etherimide)) are spun at high melt shear rates further to controlled the morphology and orientation of crystalline regions. High orientation of polymer chains and alignment of crystalline lamellar regions leads to the formation of a porous material from oriented nano-size pores that upon carbonization, with specific activation agents, produce high surface area, high microporosity activated carbon. Consequently, procedures (including parameters such as heating rate, temperature and time) were developed to properly carbonize polymer precursors. In the activation (pore creation) step, the activation kinetics, including the reactivity size of activation agents, and the homogeneity of activation system, were addressed to control the carbons texture. Interaction of carbon with hydrogen is relatively low and may reach up to 6-7 kJ/mol. Since organocyclic-CNHN macromolecules with unsaturated bonds that exhibit rigid planar configuration and are abundant in electronegative nitrogen atoms, can complex metal-salt and are enable for RT application for H₂ storage systems in moderate pressure. Thus the synthetic methods

are expanded to incorporate reactive sites into the carbon nanostructures by doping polymerized unsaturated functionalized polycyclic complexes (Melem, Fe-Melem, and Nit-Melem). Alloying activated carbon with unsaturated functionalized polycyclic complex(ed) with Melem, the proper compositions, and the ratio of carbon/alloy and other components, is needed. Also, surface modifications of the nanostructures of polymer based carbons (by blending different polymer precursors) and control of hydrogen's binding energy with the carbon/alloys have been part of this study. Extensive physisorption and chemisorptions (of H₂ adsorption) characterizations have been performed to verify the synthetic effort.

Results

In FY 2010-2011, the main focus still remains the exploration of new polymer-based materials and synthetic routes by tailoring the morphology of polymer precursor to produce high surface area, higher microporosity and small pore size nanostructured carbons. Besides our laboratories, hydrogen storage measurement has been tested at other several industrial and government facilities. The porous textures and hydrogen storage capacity at 1 bar and 77 K are summarized in Table 2. These carbons gave S_{BET} from 1,000 to 3,200 m²/g. All carbons (beside APKI-1 and APKI-4) have microporosity >90%, with average pore diameter $d_{\text{DR}} \sim 10\text{--}20 \text{ \AA}$. A hydrogen gravimetric storage capacity $W(\text{H}_2) \sim 2.98 \text{ wt\%}$ and $V(\text{H}_2) \sim 25 \text{ g/L}$ was obtained at 77K and 1 bar.

TABLE 2. Porous Texture and Hydrogen Storage Capacity (77 K, 1 bar) 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	$W(\text{H}_2)$ wt%	$V(\text{H}_2)$ gH ₂ /L
NitCP-89	420	0.21	0.19	32.8	1.40	1.14	15.29
NitACP-119	1059	0.47	0.45	10.4	1.031	2.40	24.74
NitACP-121	2188	0.94	0.88	14.1	0.694	2.98	20.68
NitACP-109	2224	0.97	0.93	13.5	0.680	2.9	19.72
NitACP-127	2530	1.10	0.99	16.0	0.625	2.86	16.75
NitACP-133	2580	1.09	1.02	16.5	0.629	2.80	17.60
NitACP-136	2802	1.16	1.10	16.4	0.602	2.66	16.01
APKI-1	3255	1.71	1.24	20.0	0.444	2.93	13.02
APKI-4	3111	1.63	1.15	19.6	0.469	2.82	13.24
ACP-113	2315	0.97	0.93	15.3	0.680	2.97	20.16
ACP-125	3010	1.38	1.15	18.23	0.532	2.98	18.06
ACP-127	2530	1.10	0.99	16.0	0.625	2.86	17.88
ACP-136	2471	1.02	0.98	15.8	0.657	2.58	16.95

A new type of polymer-based carbons that incorporate metal ions with high surface area and narrow pore size distribution were developed. Figure 1 compares the 77

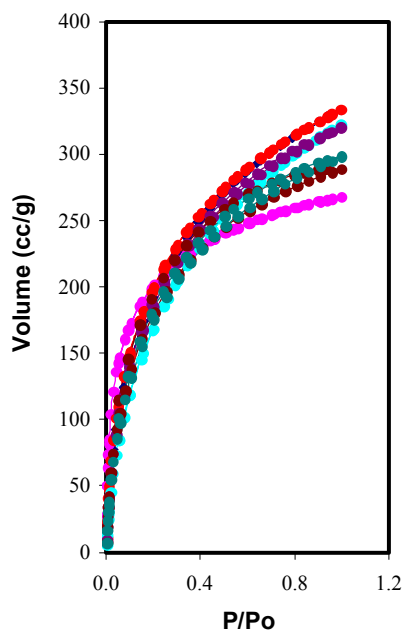


FIGURE 1. Hydrogen uptake (77 K, 1 bar) of polymer-based carbon (●) ACP-113; (●) NitACP-121; (●) ACP-127; (●) ACP-123; (●) NiACP-127; (●) ACP-136; (●) NitACP-136.

K hydrogen isotherms of nanostructured polymer-based (different polymer precursors) carbons synthesized under various conditions. Scanning electron microscope (SEM) images (Figure 2) of the carbon (NitCP-89) synthesis with metal gives nanotube structures (Figure 2a) with a diameter about 30 nm. Without metal ions, the carbon (APKI-1) shows a layer stack structure with small pores on the wall (Figure 2b). Although the BET surface area of NitCP-89 is lower at $\sim 420 \text{ m}^2/\text{g}$ compared with APKI-1 which is $3,225 \text{ m}^2/\text{g}$, the volumetric hydrogen uptake of NitCp-89 is 15.79 g/L (at 77K, 1 bar) higher than APKI-1 ($\sim 13.02 \text{ g/L}$).

Figure 3 shows a set of these carbons that were subjected to H_2 uptake at a pressure up to 20 bar at 77 K and 273 K up to 60 bar. At 273 K and 60 bar, the carbons made from phenyl phosphine oxide (NitACP-109 has $S_{\text{BET}} \sim 2,224 \text{ m}^2/\text{g}$, $V_{\text{pore}} \sim 0.97 \text{ cc/g}$ and $d_{\text{DR}} \sim 13.5 \text{ \AA}$) shows the highest volumetric hydrogen capacity $\sim 8 \text{ g H}_2/\text{L}$. However, at 77 K and 20 bar, polyether ether ether ketone (APKI-1 has $S_{\text{BET}} \sim 3,225 \text{ m}^2/\text{g}$, $V_{\text{pore}} \sim 1.7 \text{ cc/g}$ and $d_{\text{DR}} \sim 20.0 \text{ \AA}$) carbons have the same hydrogen storage capacity of $\sim 5.8 \text{ wt}\%$ at 20 bar, and 77 K.

In the past year, we continued to focus on the synthesis of nanotube multicyclic ligand carbon. These carbons carbonized at 600°C with different pyrolysis times from 2 h to 60 hours giving a different morphology than were observed by transmission electron microscope images. The surface area and hydrogen storage capacity of melem-based carbon at 77 K, 1 bar are shown in the Table 2.

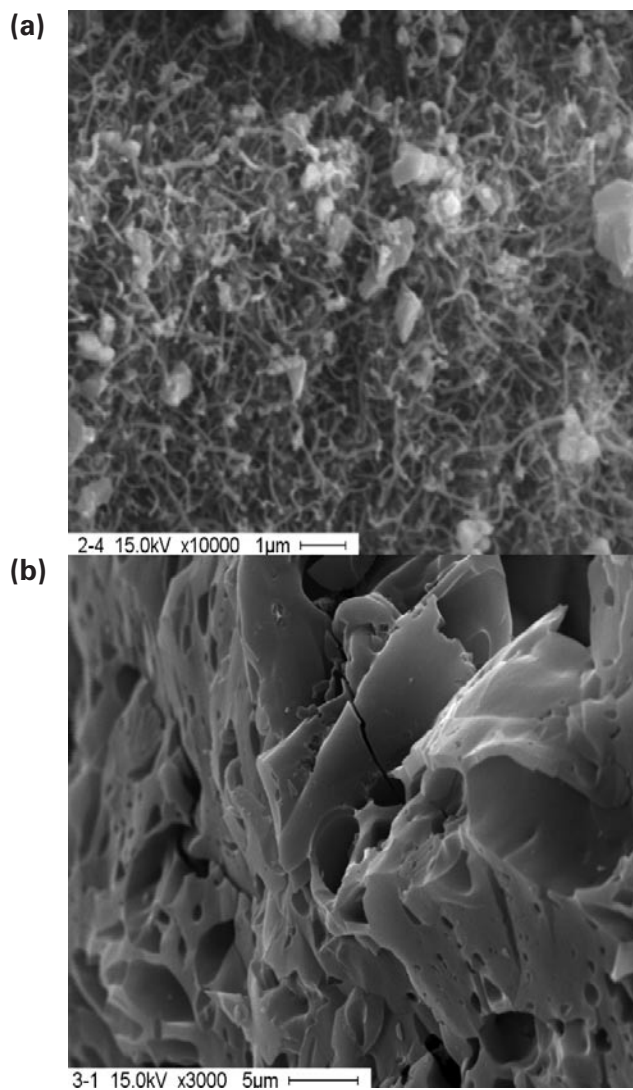


FIGURE 2. SEM image of (A) polymer-based carbon (NitCP-89) nanotube; B) activated polymer-based carbon.

TABLE 2. The Surface Area and Hydrogen Storage Capacity of Melem-Based Carbon at 1 bar, 77 K

Sample ID	S_{BET} (m^2/g)	H. C. (mL/g)
Ma015560-8	598.4	91.68
Ma015565-8	820.1	86.30
Ma015570-15	306.5	25.71
Ma015570-16	460.1	42.51
Ma015570-17	690.4	82.76
Nit70-2	189.0	23.50

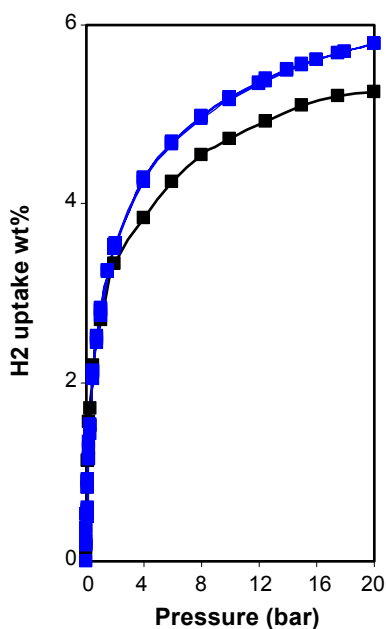


FIGURE 3. Gravimetric hydrogen uptake of APKI-1(■); PKOMe(●) at 77 K, up to 20 bar.

Conclusions

- A new type of polymer-based carbons with the incorporation of metal ions with high surface area and narrow pore size distribution were developed. The hydrogen storage capacity was ~3.0 at 77 K, 1 bar.
- Detailed study of composition and morphology of new type of carbon nanotube with Fe and other metal into organocyclic-CNHn macromolecules rich with unsaturated bonds that should be available for RT application at moderate pressures for H₂ storage systems.
- Demonstrated synthesis of modified polymer-based carbons with high surface area and low average pore width. Accomplished gravimetric storage capacity of ~6.7-7.0 wt% (77 K, 60 bar) and volumetric capacity 8 gH₂/L (237 K, 60 bar) with a high reproducibly on production in laboratory scale!

FY 2011 Presentations

1. I. Cabasso; and Youxin Yuan, "Polymer-based activated carbon for hydrogen storage", *DOE Annual Merit Review Highlights Hydrogen and Fuel Cell Projects*, port, June 9, 2011, Washington, D.C.