IV.C.3 Nanostructured Activated Carbon for Hydrogen Storage

Professor Israel Cabasso (Primary Contact)
and Dr. Youxin Yuan
State University of New York (SUNY)
Polymer Research Institute (esf), Syracuse Campus
1 Forestry Drive
Syracuse, NY 13210
Phone: (315) 470-6857; Fax: (315) 470-6920
E-mail: icabasso@syr.edu

DOE Technology Development Manager:
Monterey R. Gardiner
Phone: (202) 586-1758; Fax: (202) 586-9811
E-mail: Monterey.Gardiner@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Technical Advisor: Scott Salvati
Phone: (303) 275-4776; Fax: (303) 275-4753
E-mail: Scott.Salvati@go.doe.gov

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PoroGen, LLC, Boston, MA

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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 gH_2/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 section (3.3.4) outlined in the Hydrogen, Fuel Cells and Infrastructure 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. 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

Accomplishments

- Established the correlation of structures (surface area and micropore volume) of the carbons with hydrogen storage capacity; an average surface coverage ~16.0 μg H_2/m^2 and hydrogen density in pores ~0.055 g/cm^3 has been achieved.
- Synthetic method for incorporation of unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem) has been developed, and hydrogen binding energy has been improved to ~14 kJ/mol.
- Achieved synthesis of modified polymer-based carbons with high surface area (up to 4,000 m^2/g) and low average pore width (down to 8.5 Å).
- Achieved a durability of hydrogen storage on high surface area poly(ether ether ketone) (PEEK)

carbon >30 cycles with gravimetric storage capacity of ~6.7-7.4 wt%, and volumetric capacity of ~45 g/L at 77 K and 5-6 MPa.

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Introduction

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 micro porous structure (pore width ~7-20 Å). The high surface area of the polymeric precursor aids in preparation of this unique carbon (Bruner-Emmett-Teller [BET] specific surface area [S_{BET}] >3,000 m^2/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 as to produce carbon with the designed morphology for activation to high surface area and controlled micropores. Thus, polymer precursors such as modified poly(phenylene oxide), modified PEEK, and 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 as to control the carbons texture. The synthetic methods are expanded to incorporation reactive sites into the carbon nanostructures by doping polymerized unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem) or modification of carbon surface by solvent/polymer carbon alloy. Extensive physisorption and chemisorption (H_2 adsorption) characterizations have been performed to verify the synthetic effort.

Results

In Fiscal Year 2009, the main focus remained exploration of new materials and synthetic routes by tailoring the morphology of polymer precursor to produce high surface area, higher microporosity and small pore size nanostructured carbons. More than 100 batches of polymer-based nanostructured carbons were synthesized and screened. Figure 1 illustrates the correlation of surface area with hydrogen storage capacity at 77 K and 0.1 MPa. Two distinct regions were observed. For carbon with S_{BET} ≤1,300 m^2/g, hydrogen adsorption increases linearly with S_{BET}, up to $W_{ad.H2}$ ~2.7 wt%, at an average surface coverage ~16.0 µg H_2/m^2. For the carbons with S_{BET} >1,300 m^2/g, the hydrogen uptake overall shows a modest increase with surface area. The variation of hydrogen uptake at 77 K and 0.1 MPa with total pore volume was presented in Figure 2. The hydrogen uptake is shown to increase with pore volume, but with great scatter. The calculated hydrogen density in pores varies from 0.013 g/cm^3 to 0.055 g/cm^3. The hydrogen storage on these carbons has been tested for more then 30 cycles, and shows no decrease of the absorption capacity.

Hydrogen uptakes of these carbon nanostructured materials were also tested at independent institutions and national laboratories. For example: a typical

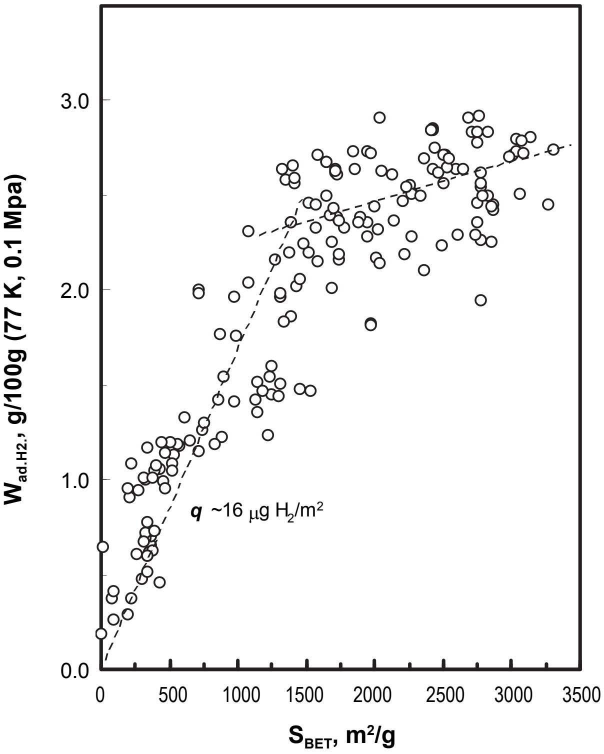

FIGURE 1. The dependence of hydrogen adsorption at 77 K and 0.1 MPa on BET surface area.

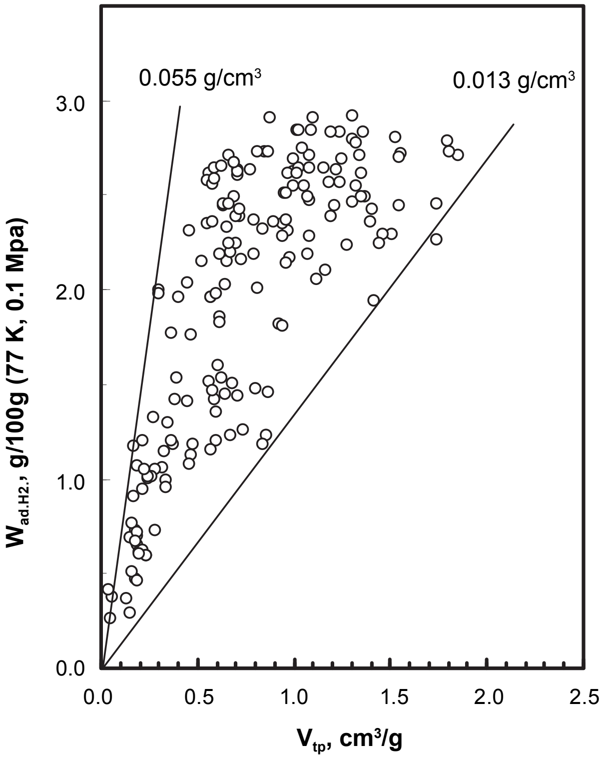

FIGURE 2. The dependence of hydrogen adsorption at 77 K and 0.1 MPa on total pore volume   obtained from nitrogen sorption.

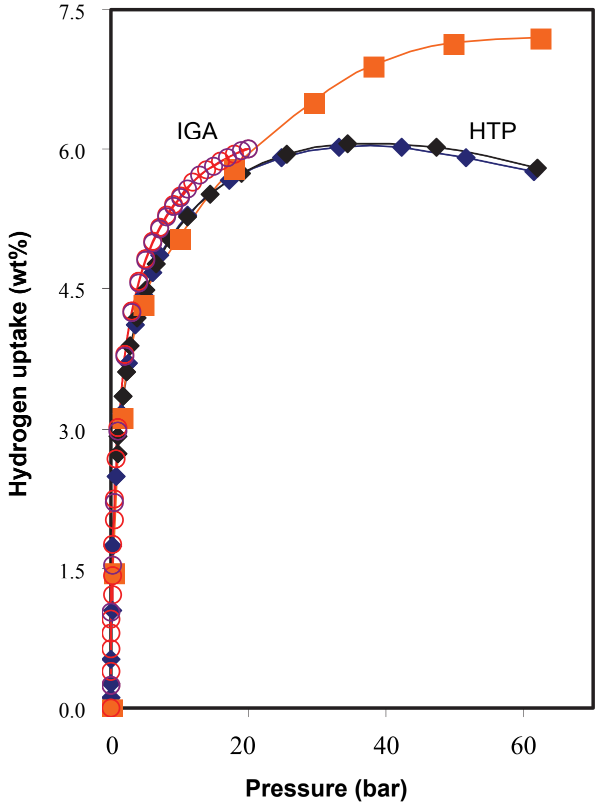

FIGURE 3. Hydrogen isotherms of MPK/PI-12 and MPK/PI-6 polymer-based carbons measured gravimetrically (IGA instrument, pressure up to 20 bar) and volumetric technique (HTP instrument, pressure up to 60 bar). Measurements done at Hiden Isochema Ltd., U.K.

hydrogen isotherms of polymer-based carbon (MPK/PI-12) shown in the Figure 3 is measured gravimetrically on an intelligent gravimetric analyzer (pressure up to 20 bar) and volumetric technique on a high temperature pressure instrument (pressure up to 60 bar) (measurements were done at Hiden Isochema Ltd.). The results of hydrogen uptake of these carbon materials are summarized in Table 2. At 77 K and pressure of 6 MPa, the hydrogen gravimetric storage capacity, W(H_2) up to 7.4 wt% has been achieved by MPK/PI-6 at 77 K and 60 bar. And 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 MPK-1 (measurements by GTI, Chicago).

The hydrogen binding energy for all carbons shown here are about -5 kJ/mol. A strategy for increasing hydrogen binding energy has been executed by introducing a large number of certain ionic sites to polymer framework. In the past year, a set of trace-organometallics (Ni) and multiheterocyclic ligand compounds that were first modelled as dopant by the Parametric Model number 3 computational method. The Melem [$C_6N_7(NH_2)_3$] which has a planar configuration that resembles a graphite structure and is rich in electronegative nitrogen element was chosen to dope within a high surface area carbon by polycondensation reaction of carbon-nitrogen-hydrocarbon monomers at elevated temperature. The melem-doped carbon exhibits a highly microporous nature. The pore size distribution histogram of this carbon (Figure 4) reveals that all the pores fall within the micropore region (pore diameter <20 Å). Comparison of the pore size distribution prior to and after doping clearly shows that after doping, the pore size distribution shifted to the sub-nano pore region, producing a significant portion with pores below 10 Å in diameter. The melem-doped carbon shows a sharp increase in hydrogen binding energy up to 14 kJ/mol at low hydrogen loading (Figure 4).

In addition to doping organocyclic $-CNH_n$ macromolecules to high surface area carbon to increase hydrogen bind energy, solvated carbon alloyed method was also employed to substantially increase the H_2 storage temperature. Table 3 is preliminary results of the hydrogen storage capacity and storage temperature by solvent-carbon alloys, which seems to greatly enhance the storage capacity at elevated temperatures under certain conditions. A gravimetric storage capacity of up to 6.3 wt%, and a volumetric storage capacity of up to ~36 g H_2/L have been recorded at > ~137 K by highly porous carbon, e.g., PEEK/PEI-11 alloys.

TABLE 2. Hydrogen Storage Capacity of Polymer-Derived Carbon Nanostructures

Sample	S_{BET}	V_{tp}	H_2 Uptake at 77K							
			0.1 MPa		1 MPa		2 MPa		6 MPa	
	(m^2/g)	(cm^3/g)	g/100g	g/L	g/100g	g/L	g/100g	g/L	g/100g	g/L
MPK-1	1,800	0.84	2.0	14	3.5	26	4.5	34	5.8	43-46
MPK-2	1,760	0.74	2.1	17	3.0	24	3.3	26	4.4	35
MPK-3	2,000	0.90	2.4	17	3.5	25	3.7	26	4.5	32
MPK-4	2,300	0.97	2.6	18	3.9	26	4.3	29	5.1	35
MPK-5	2,720	1.15	2.7	16	4.4	26	4.9	29	5.8	35
MPK/PI-1	2,110	1.03	2.8	18	4.5	29	4.8	31	5.0	33
MPK/PI-2	2,430	1.03	2.8	18	4.4	29	4.8	31	4.7	31
MPK/PI-3	2,775	1.28	2.7	15	4.7	26	5.3	30	5.4	30
MPK/PI-4	2,890	1.29	2.6	14	4.7	26	5.3	30	6.4	36
MPK/PI-5	2,935	1.36	2.6	13	4.5	24	5.1	27	5.9	31
MPK/PI-6	3,035	1.81	2.5	11	5.1	22	5.9	26	7.4	32
MPK/PI-7	3,095	1.60	2.7	12	4.8	22	5.5	26	6.4	30
MPK/PI-8	3,160	1.98	2.8	11	5.0	20	5.9	24	7.0	28
MPPO-1	3,920	2.20	2.7	10	4.8	18	5.3	20	6.4	24

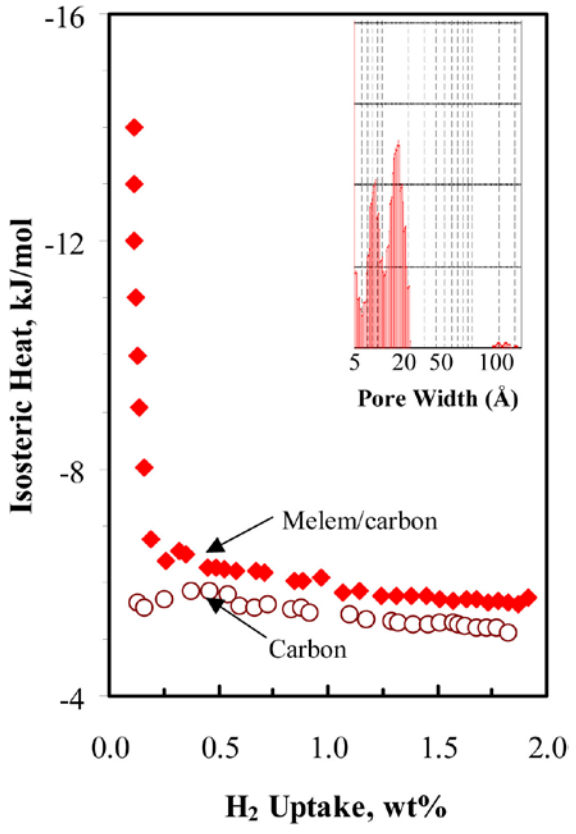

FIGURE 4. Hydrogen binding energy of carbon (○) and Melem-doped carbon (♦). (Insert is pore volume distribution histogram of melem doped carbon.)

Conclusion and Future Direction

- Established correlation of hydrogen storage capacity with carbon structure (surface area and micropore volume).
- Achieved a gravimetric storage capacity ~7.4 wt% and volumetric capacity ~46 g/L at 77 K on nanostructured carbons, and a ~6.3 wt% gravimetric storage capacity at 138 K by solvent/polymer-carbon alloy method.
- Achieved a durability of hydrogen storage on high surface area PEEK carbon more than 30 cycles without decrease in hydrogen adsorption.
- Enabled doping on higher surface area carbon with organometallic compounds that exhibit rigid planar configuration and are rich of electronegative nitrogen atoms, $[CNH]_n$, and increased hydrogen binding energy up to ~14 kJ/mol.
- Continue to develop, modify, characterize and scale-up production of nanoporous polymer materials and carbons.
- Improving hydrogen binding energy by surface modification and doping with heterocyclic and heteroaromatic polymers and with trace organo catalysts.

TABLE 3. Hydrogen Storage of Solvent - Nanostructured Carbon Alloy of Various Porous Textures

Carbon	Porous Texture				Hydrogen Storage		
	S_{BET} (m^2/g)	V_{mp} (mL/g)	V_{tp} (mL/g)	d_{DR} (Å)	T_{de} (°K)	W_{H2} (wt %)	V_{H2} (g H_2/L)
BP2000	1,560	0.70	2.07	-	-	-	-
MPK-5	2,720	1.10	1.15	17.2	137	6.3	31.4
MPK/PI-10	2,710	1.20	1.29	18.6	137	5.6	27.9
MPK/PI-11	3,300	1.46	1.85	19.0	138	7.2	35.9

FY 2009 Publications and Presentations

1. Y. Yuan; I. Cabasso; and H. Liu, "Surface Morphology of Nanostructured Polymer-based Activated Carbons", *J. Physical Chem. B*, **2008**, 112, 1364.

2. S. Li, X. Wang, Y. Yuan, I. Cabasso, "Synthesis of Polymer-Based Activated Carbons and Their Hydrogen Uptake," submitted to *Chemistry Materials*, 2009.

3. I. Cabasso; Xinwei and Youxin Yuan, "Polymer-based activated carbon for hydrogen storage", *DOE Annual Merit Review Highlights Hydrogen and Fuel Cell Projects*, Poster, May 18-22, 2009, Crystal City, VA.