IV.C.2 Nanostructured Activated Carbon for Hydrogen Storage

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

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

DOE Project Officer: Jim Alkire
Phone: (303) 275-4795
E-mail: James.Alkire@go.doe.gov

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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, 2010)

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 (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 Hydrogen Program 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 (** Data is based on material only, not system value)

Storage Parameter	Units	2015 System Target	SUNY-Syracuse**
System Gravimetric Capacity	kWh/kg (wt% H_2)	1.8 (5.5)	2.4 (7.2)
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

Accomplishments

- Demonstrated synthesis of a modified polymer-based carbon 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 ~6.7-7.0 wt%, and volumetric capacity of ~43-45 g/L at 77 K, 5-6 MPa.
- Achieve a high reproducibly on production in laboratory scale.
- Introduction of a carbon alloy with organocyclic-$(CNH)_n$ macromolecules rich with *unsaturated bonds* that should be available for room temperature (RT) application at moderate pressures for H_2 storage systems. The melamine derivative carbonized or incorporating to the activated carbon

without the metal predicated at 77 K and 1 bar is 4-5 wt% with surface area ~2,000 m^2/g.

- Using theoretical simulations (Monte Carlo computation) to obtain configurations of Melon (and g-C_3N_4) with d-transition metals (Mg, Ti, V, Ni, Fe) indicating that the complex structures with these metals can increase the hydrogen adsorption and with desirable binding energy.

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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 micro porous structure (pore width ~7-20 Å). The high surface area of the polymeric precursor aids in preparation of this unique carbon (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 to produce carbon with the designed morphology for activation to high surface area and controlled micropores. Thus, polymer precursors (modified poly(phenylene oxide), modified poly (ether ether ketone [PEEK]), polyetherimide [PEI]) 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 abound in electronegative nitrogen atoms, can complex metal-salt and are enabled for RT application for H_2 storage systems at moderate pressure. Thus the synthetic methods are expanded to incorporate reactive sites into the carbon nanostructures by doping polymerized unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem). Also, melamine derivatives have been synthesized and carbonized for adsorption of hydrogen. Alloying activated carbon with unsaturated functionalized polycyclic complex(ed) with Melem, F-Melem, and/or traces of Ni, Ti, Fe-Melem have been accomplished. Finding 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 chemisorption (H_2 adsorption) characterizations have been performed to verify the synthetic effort.

Results

In Fiscal Year (FY) 2010, the main focus still 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. The hydrogen storage measurement has been tested at several laboratories. Figure 1 shows hydrogen uptake isotherms (excessive uptake) of polymer-based carbons measured gravimetrically (pressure up to 20 bar), and volumetrically high throughput (instrument pressure up to 60 bar) (measurement by *HidenIsochema Co. U.K*). The hydrogen uptake reaches 6.6 wt% for APKI-S6 at 50 bar, and for carbon 5.5 wt% 20 bar (as measured with both techniques). The APKI polymer-carbons are PEEK/PEI, and poly(2,6-dimethyl-1,4-phonylene oxide)-based carbon (APPO) is derivative of phenyl phosphine oxide. Surface areas for APKI6S2-N4, APPO-R8, APKI-S6 and APKI6S2-N20 are recorded as 3,070, 2,550, 3,034, 3,160 m^2/g, respectively.

Figure 2 shows excessive hydrogen uptake of polymer-based carbons (PEEK, PEEK/PEI and APPO) at higher pressures evaluated at different testing laboratories.

The hydrogen binding energy for all carbons shown here are ~5-6 kJ/mol. A strategy for increasing hydrogen binding energy has been executed by introducing a large number of certain metal sites to polymer framework. In the past year, a set of Melon configurations, and Melon with Mg, Fe, Ti, V, Ni single metal atoms were first modeled by Monte Carlo computational method at 300 K. These models indicate that Ti and Mg do not only interact with the melon units but also "open" the spacing for hydrogen (up to four for Ti and two for Mg) which were situated here at the local

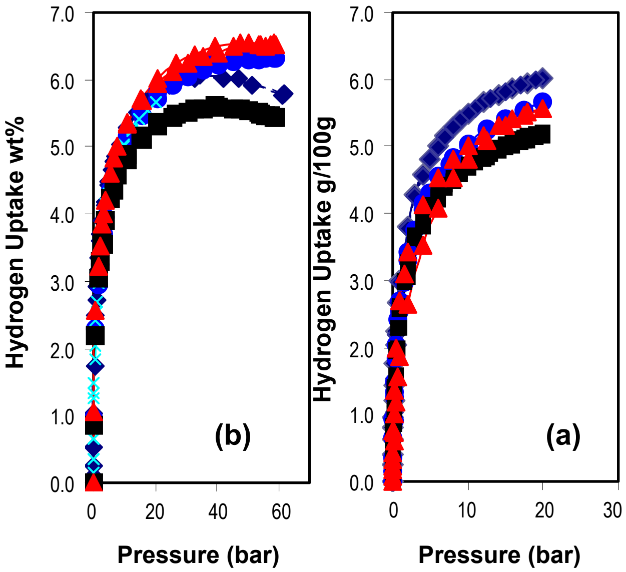

FIGURE 1. Hydrogen uptake isotherms (excessive uptake) of polymer-based carbons measured gravimetrically (pressure up to 20 bar), and volumetrically high throughput (instrument pressure up to 60 bar). The hydrogen uptake reaches 6.6 wt% for APKI-S6 at 50 bar, and for carbon 5.5 wt% 20 bar (as measured with both techniques) APKI6S2-N20 (◆), APKI6S-N4 (●), APKI-S6 (▲), APPO-R8(■). Measurements done at HidenIsochema Co. U.K

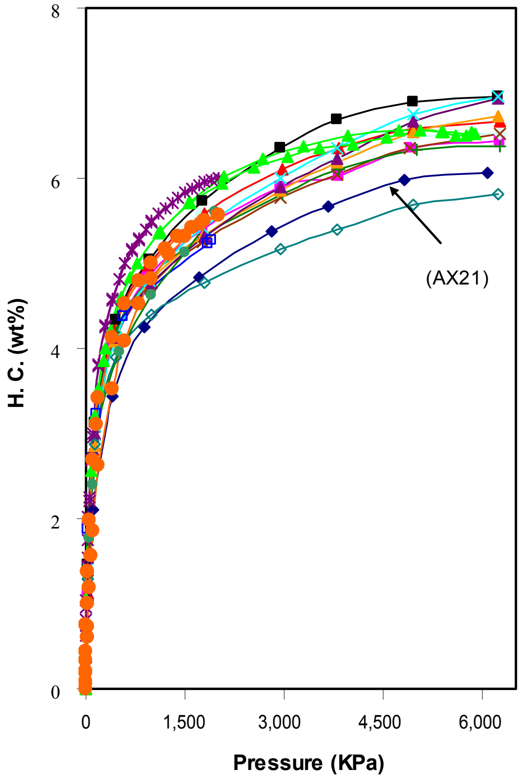

FIGURE 2. Excessive hydrogen uptake of polymer-based carbons (PEEK, PEEK/PEI and APPO) at higher pressures. (Evaluations were conducted by five different testing laboratories.)

minimum potential (energy) configuration; where in the case of Ni the metal was found to be competing on the position and "close" the space for hydrogen molecules, which were found the minimum out of the melon units. Metal clusters M(n) (not shown here) are used to model "real" possible events. The Melon with different metal catalysts was carbonized at 700°C from C-N nano tubing with diameter ~12 nm traces of large cluster aggregation of Fe (Figure 3A). Figure 3B shows lattice structure formed on wall of this carbon. The electro diffraction gives a distance of 3.4 Å hydrogen adsorption of carbonized Melon carbon nano-tubing before complex with metal at 87 K and 1 bar is shown in Figure 4. All the samples have surface areas below 650 m^2/g. The hydrogen adsorption increases linearly with the surface area. (Uptake about ~3 wt% hydrogen can be obtained by extrapolating to the surface area ~1,000 m^2/g).

Conclusion

- Accomplished synthesis of a 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). The gravimetric storage capacity of these carbons achieved ~6.7-7.0 wt%, and volumetric capacity of ~43-45 g/L at 77 K, 5-6 MPa!!
- Achieve a high reproducibly on production of these carbons in laboratory scale!!
- Organocyclic-(CNH)$_n$ macromolecules rich with unsaturated bonds that should be available for RT

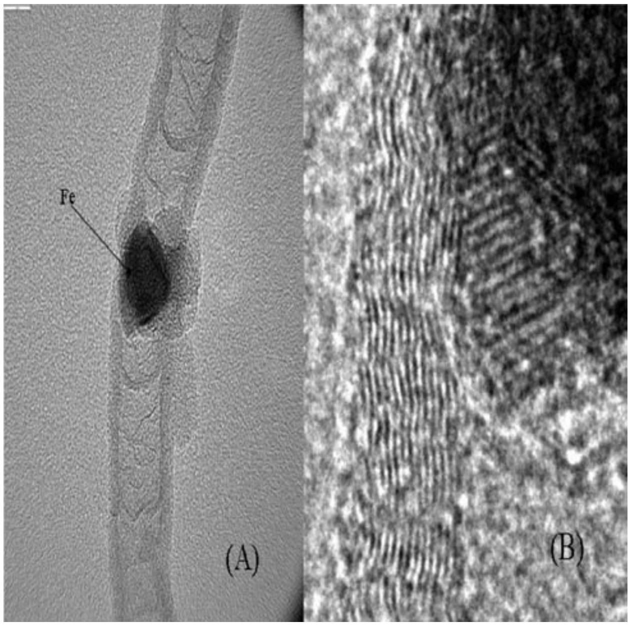

FIGURE 3. Transmission electron microscopy image of carbonized Melon. The Melon carbonized at 700°C form C-N nano tubing with diameter ~12 nm (A). The lattice structure formed on wall of this carbon and Fe site (B).

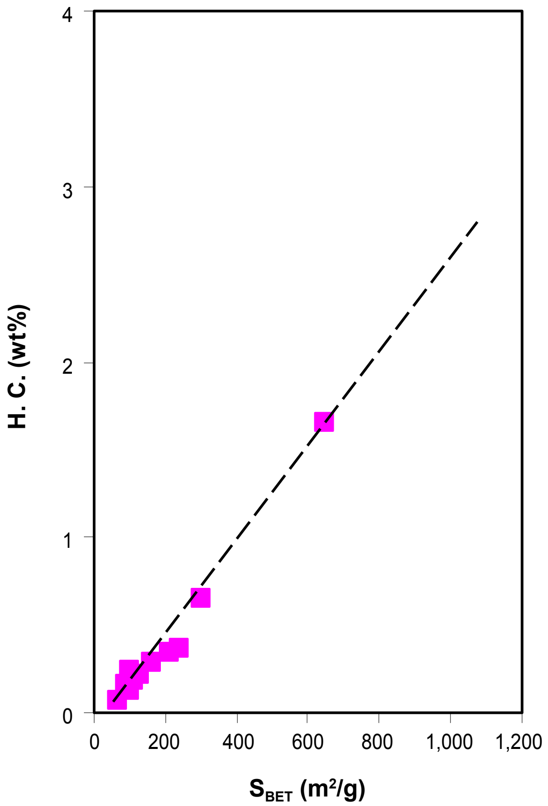

FIGURE 4. Hydrogen adsorption of carbonized Melon carbon nanotubing before complex with metal at 87 K and 1 bar.

application at moderate pressures for H_2 storage systems has been established. The hydrogen storage of the melamine derivative carbonized or incorporating to the activated carbon without the metal predicated at 77 K and 1 bar is 4-5 wt% with surface area ~2,000 m^2/g.

- Using theoretical simulations (Monte Carlo computation) to obtain configurations of Melon (and g-C3N4) with d-transition metals (Mg, Ti, V, Ni, Fe) indicating that the complex structures with these metals can increase the hydrogen adsorption and with desirable binding energy.

FY 2010 Publications and Presentations

1. I. Cabasso; and Youxin Yuan, "Polymer-based activated carbon for hydrogen storage", *DOE Annual Merit Review Highlights Hydrogen and Fuel Cell Projects*, Presentation, June 9, 2010, Washington, D.C.