Polymer-Based Activated Carbon Nanostructures for H₂ Storage

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The Michael Szwarc Polymer Research Institute of the State University of New York-esf (Syracuse) and PoroGen LLC have collaborated in an effort to develop polymer-based nanostructured carbons:

- High BET surface area > 2600 m²/g;
- High microporosity > 95%;
- Average pore size ~ 10 Å;
- Hydrogen uptake: ~ 7 wt% and 45 g H₂/L at elevated Temperature;
- Increasing hydrogen storage temperature by introduction of active sites in the carbons with polycyclic triazine rings (poly-melem).
Overview

Timeline

- Start - May 2005
- End - April 2010
- 65% Completed (due to DOE’s budget shortage)

Budget

- Total project funding
  - DOE - $1,543,420
  - Cost Share: $391,767 (20%)
- Total funding received in FY 2008
  - $300K
- Funding for FY 2009
  - $250K

Barriers

- Improved Gravimetric and volumetric density of H₂ uptake
- Controlled matrix doping and polymers compatibility
- Improved heat H₂ of adsorption

Partners

PoroGen (Boston MA)

collaborations:
- GTI (Chicago)
- {several national labs and research institutions for high pressure testing}
### Project Objectives/Relevance

**Overall**

Develop and demonstrate reversible nanostructured polymer-based carbon on hydrogen storage materials with materials-based volumetric capacity of 50 g H$_2$/L, with potential to meet DOE 2010 system-level targets.

<table>
<thead>
<tr>
<th>Performance Measure</th>
<th>June, 2008 – May, 2009 performance Target</th>
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</thead>
<tbody>
<tr>
<td>Carbon Surface Area and Pore Volume</td>
<td></td>
</tr>
<tr>
<td>$S_{BET} &gt; 3000$ m$^2$/g</td>
<td></td>
</tr>
<tr>
<td>$V_{mp} &gt; 1.4$ cc/g</td>
<td></td>
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<tr>
<td>Hydrogen Storage Capacity</td>
<td></td>
</tr>
<tr>
<td>Gravimetric Capacity (Material Based)</td>
<td></td>
</tr>
<tr>
<td>$&gt;6$ wt%</td>
<td></td>
</tr>
<tr>
<td>Volumetric Capacity (Material Based)</td>
<td></td>
</tr>
<tr>
<td>$&gt;40$ g/L</td>
<td></td>
</tr>
<tr>
<td>Durability of Hydrogen Storage on Carbon</td>
<td>$&gt; 30$ cycle</td>
</tr>
<tr>
<td>Incorporation of Unsaturated Functionalized Polycyclic Complexes (Melem, F-Melem, Ni-Melem)</td>
<td>$&gt; 20$ wt% on Carbon</td>
</tr>
<tr>
<td>Improve Hydrogen Binding Energy</td>
<td>$&gt;&gt;12$ kJ/mole</td>
</tr>
</tbody>
</table>
## Technical Approach

### Task 1: Processing Precursors
- Material Development
- Modification
- Characterization

- Processing polymer precursors (MPPO, MPEEK and PEI) and high melt shear rate Controlling morphology and crystalline orientations

80% complete

### Task 2: Nanostructured Carbon Preparation
- Prepare high surface area activated polymer based carbon
- Analysis morphology (surface area, porosity, pore volume and size distribution)
- Production scale up

70% complete

### Task 3: Hydrogen Storage (Physisorption & Chemisorptions)
Incorporating reactive sites into the carbon nanostructures.

- Incorporation and polymerization of unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ni-Melem) rich in double bonds with a reduction factor of 10-50 kJ/mol (chemical interaction binding energy is a function of pressure, temp. and trace of co-catalyst Fe, or Ni).

60% complete

### Task 4: Hydrogen Storage Testing
- Testing hydrogen adsorption the temp. range: 77K-300K and pressure of: 0.1 to 60 bar
- Testing durability of material in repeated runs.

50% complete

**Note:** Tasks 1 and 2 have been designed to modify high performance polymer-based nanostructure carbon material to fit Task 3.
Nanostructured Activated Polymer Carbon Preparation Methodology

**Polymer Precursor**
- Modification: stabilization, crosslinking

**Carbonized Polymer**
- Carbonization: temperature, heating rate, time

**Melem/Carbon**
- Alloyed/ and Polymerizing:
  - Poly-Melem
  - F-Melem
  - Ni-Melem

**Activated Carbon**
- Activation: activation agent, temperature, homogeneity
Correlation of Surface Area with Pore Size of Activated Polymer Carbons

Target: $S_{\text{BET}} > 2600 \text{ m}^2/\text{g}$ with average pore width $\sim 8 \text{ Å}$

Achieved: $S_{\text{BET}} \sim 1850 \text{ m}^2/\text{g}$ with average pore width $\sim 8 \text{ Å}$

$S_{\text{BET}} \sim 3000 \text{ m}^2/\text{g}$ with average pore width $\sim 18 \text{ Å}$
(A). The structure and ordering can be controlled with agumentation of carbonization temperature. The structure ordering also narrows the pore size distribution.

(B). Increase activation temperature (up to 800°C) leads to broadened pore size distribution, increases surface area and larger average pore diameter.

Pore Size Distribution as Function of Temperature
For carbon with $S_{\text{BET}} \leq 1300$ m$^2$/g, the gravimetric capacity increases linearly with $S_{\text{BET}}$ at average surface coverage $\sim 16\mu g/H_2$.

For carbon with $S_{\text{BET}} \geq 1300$ m$^2$/g shows a modest increase in hydrogen uptake up to $W_{H_2} \sim 3.0$ wt%.

The hydrogen density in pores varies from 0.013 g/cm$^3$ to 0.055 g/cm$^3$. 
a. Unite surface area hydrogen uptake at 77K and 1 bar achieved average surface coverage 21.9 \( \mu \text{g/m}^2 \) at pore size \(~8\text{Å}~

b. The hydrogen density in pores at 77 K and 1bar achieved ~0.055 g/cm\(^3\) (80% coverage).

d. Isosteric heat of adsorption, \(Q(H_2)\) is \(5 - 6 \text{ kJ/mol}\), and 10 kJ/mol at lower pressure.
Correlation of Hydrogen Capacity with Surface Area at High Pressure and 77K

- Hydrogen uptake at 77K on polymeric carbon follows Langmuir adsorption.

- The correlation between hydrogen uptake and surface area $S_{\text{BET}}$ (with at various $H_2$ pressure) increases linearly.
Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_\text{IR}$ (cm$^3$/g)</th>
<th>0.1 g/100g MPa</th>
<th>1MPa g/100g</th>
<th>2MPa g/100g</th>
<th>6MPa g/100g</th>
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<tbody>
<tr>
<td>MPK-1</td>
<td>1800</td>
<td>0.84</td>
<td>2.0</td>
<td>14</td>
<td>3.5</td>
<td>26</td>
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<tr>
<td>MPK-2</td>
<td>1760</td>
<td>0.74</td>
<td>2.1</td>
<td>17</td>
<td>3.0</td>
<td>24</td>
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<tr>
<td>MPK-3</td>
<td>2000</td>
<td>0.90</td>
<td>2.4</td>
<td>17</td>
<td>3.5</td>
<td>25</td>
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<tr>
<td>MPK-4</td>
<td>2300</td>
<td>0.97</td>
<td>2.6</td>
<td>18</td>
<td>3.9</td>
<td>26</td>
</tr>
<tr>
<td>MPK-5</td>
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<td>1.15</td>
<td>2.7</td>
<td>16</td>
<td>4.4</td>
<td>26</td>
</tr>
<tr>
<td>MPK/PI-1</td>
<td>2110</td>
<td>1.03</td>
<td>2.8</td>
<td>18</td>
<td>4.5</td>
<td>29</td>
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<tr>
<td>MPK/PI-2</td>
<td>2430</td>
<td>1.03</td>
<td>2.8</td>
<td>18</td>
<td>4.4</td>
<td>29</td>
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<tr>
<td>MPK/PI-3</td>
<td>2775</td>
<td>1.28</td>
<td>2.7</td>
<td>15</td>
<td>4.7</td>
<td>26</td>
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<tr>
<td>MPK/PI-4</td>
<td>2890</td>
<td>1.29</td>
<td>2.6</td>
<td>14</td>
<td>4.7</td>
<td>26</td>
</tr>
<tr>
<td>MPK/PI-5</td>
<td>2935</td>
<td>1.36</td>
<td>2.6</td>
<td>13</td>
<td>4.5</td>
<td>24</td>
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<tr>
<td>MPK/PI-6</td>
<td>3035</td>
<td>1.81</td>
<td>2.5</td>
<td>11</td>
<td>5.1</td>
<td>22</td>
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<tr>
<td>MPK/PI-7</td>
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<td>1.60</td>
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<td>11</td>
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<td>20</td>
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<td>MPPO-1</td>
<td>3920</td>
<td>2.20</td>
<td>2.7</td>
<td>10</td>
<td>4.8</td>
<td>18</td>
</tr>
</tbody>
</table>

The gravimetric hydrogen storage capacity achieved ~7.0 wt% at 77K 60 bar.

The volumetric hydrogen storage capacity achieved ~ 40-45 g/L at 77 K 60 bar.
Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures

a. Gravimetric hydrogen uptake increases linearly with surface area, at a rate of ~ 20 μg H₂/(m²/g), which indicates ~ 6 H₂ molecules occupy 20 graphene hexagon units.

b-c. High volumetric hydrogen uptake (up to 46 g H₂/L) is achieved at V_{mp} ~ 0.8-0.9 mL/g.
Reproducibility of Carbon Nanostructures Synthesized from Two Different Batches of MPK/PI Blend precursor

<table>
<thead>
<tr>
<th>Batch of Material</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{mp}$ (mL/g)</th>
<th>$V_p$ (mL/g)</th>
<th>$d_{DR}$ (Å)</th>
<th>$W(H_2)$, wt% 77 K</th>
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<tbody>
<tr>
<td>1</td>
<td>3070</td>
<td>1.23</td>
<td>1.82</td>
<td>20.1</td>
<td>6.7</td>
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<tr>
<td>2</td>
<td>3365</td>
<td>1.29</td>
<td>1.99</td>
<td>19.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Poly - Melem Alloyed With Polymer Carbons

Fluorination

Ni- poly Melem-F
((tri-triazine rings)

Activated Carbons unit-cell

alloyed
(Trace quantity of co-catalyst Ni, Fe)

Melem
F-Melem
Ni-Melem

0 16 32 48 64 80

2θ (Degree)

Intensity (a.u.)
Formation and Characterization of Melem/Carbon

TGA Monitoring of Melem and $[\text{CNH}]_n$ formation within the Carbon

CP-MAS $^{13}\text{C}$-NMR
(a) The Melem/carbon registered gravimetric capacity of ~ 5.2 wt%, 1.12 wt% and 0.32% at 77 K, 195 K, and 298 K, respectively. The equivalent volumetric capacities were ~39 g/L, 8.3 g/L, and 2.4 g/L.

(b) AlloIED carbon with Melem or fluorinated Melem raises the hydrogen binding energy up to 14 kJ/mol at low pressure.
Hydrogen Storage by Solvated – Carbon Alloyed Method greatly increases the storage capacity at elevated temperatures.
### Hydrogen Storage of Solvent - Nanostructured Carbon Alloy of Various Porous Textures

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Porous Texture</th>
<th>Hydrogen Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_{\text{BET}}$ (m$^2$/g)</td>
<td>$V_{\text{mp}}$ (mL/g)</td>
</tr>
<tr>
<td>BP2000</td>
<td>1560</td>
<td>0.70</td>
</tr>
<tr>
<td>MPK-5</td>
<td>2720</td>
<td>1.10</td>
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<tr>
<td>MPK/PI-9</td>
<td>2040</td>
<td>0.94</td>
</tr>
<tr>
<td>MPK/PI-1</td>
<td>2120</td>
<td>0.98</td>
</tr>
<tr>
<td>MPK/PI-10</td>
<td>2710</td>
<td>1.20</td>
</tr>
<tr>
<td>MPK/PI-11</td>
<td>3300</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPK/PI-12</td>
<td>3530</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MPK/PI-13</td>
<td>4020</td>
<td>1.75</td>
</tr>
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</tbody>
</table>

A gravimetric storage capacity of up to 8.0 wt%, and a volumetric storage capacity of up to ~ 40 g H$_2$/L have been accomplished at above dry ice temperature by highly porous carbon, e.g., PEEK/PEI-12 alloy.
Project Summary

**Approach:** Formulated synthetic strategies toward polymer-based nanostructured carbons of controllable porosity and surface area from polymer precursors that would be alloyed with organo-active sites

Established correlation of hydrogen storage with surface area, pore size and porosity with can be alloyed with active sites.

**Technical Accomplishments and Progress:**

Demonstrated synthesis of a modified polymer based carbons with high surface area (up to 4000 m²/g) and low average pore width (down to 8.5 Å); Accomplished gravimetric storage capacity of ~ 6.7-7.4 wt%, and volumetric capacity of ~ 45 g/L at 77 K, 5 - 6 MPa

**Introduction of a carbon alloy with organocyclic-CNHₙ macromolecules rich with unsaturated bonds**, that exhibit rigid planar configuration and are rich in electronegative nitrogen atoms, that may enable application for RT and moderate pressure H₂ storage systems at high temperature. (note, the interaction with cyclic bonds may reach 100 kJ/mol, that too much, controlling and monitoring the interaction binding energy is being work on.).

A solvent/polymer-carbon alloy method has been developed for enhanced hydrogen storage at ambient temperatures (-25 °C). A total H₂ gravimetric storage > 7.0 wt% (based on carbon) and volumetric storage capacity ~ 40 g H₂/L has been achieved in preliminary experiments on nanostructured carbons, at -25 °C.
Future work

We concur that the carbon matrix by itself has a slim chance (if at all) to produce a heat of interaction, of about 20-25 kJ/mol, that is needed for an effective sorption of hydrogen at ambient temperature. Keeping this in mind our future work includes:

- **Improving the binding of hydrogen (adsorption)**
  - Alloying activated carbon with Unsaturated Functionalized Polycyclic Complexes (e.g., Melem, Fluorinated-Melem, and Ni-Melem). Finding the proper composition for the ratio of carbon/alloy and other components needed.
  - Surface modification of the nanostructures of polymer based carbon by blending different polymer precursors. Control of the binding energy of hydrogen with carbon/alloy.

- **Explore nanostructures**
  - Continue to develop, modify, and characterize polymer materials.
  - Continue to develop Nanoporous carbons.

- **Hydrogen adsorption tests** at elevated temperature of organo PEEK carbons.