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 nano structural 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;
- Increasing hydrogen storage temperature by doping carbons with multicyclic ligands.
DE-FG36-05GO15009

Overview

Timeline

- Start - May 2005
- End - April 2009
- 50% Completed (due to DOE’s budget shortage)

Budget

- Total project funding
  - DOE - $1,543,420
  - Cost Share: $391,767 (20%)
- Total funding received by FY 2007
  - $430K
- Funding received for FY 2007
  - $230K

Barriers

- Polymer compatibility
- Controlled doping
- High temperature tests

Partners

PoroGen (Boston MA)
Project Objectives

Overall

Develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with materials-based volumetric capacity of 50 g H₂/L, with potential to meet DOE 2010 system-level targets.

FY2007 - 2008

- Develop polymer-based nanostructured carbons with high surface area and high micropore volume;
- Demonstrate reproducibility of 10-gram scale batch production of high surface area carbon;
- Characterize hydrogen storage capacity under various pressure and temperature conditions. Target for 2007 > 6 wt% and 40 g/L of material-based H₂ capacity;
- Develop methods for organometallic and multicyclic ligand-doped polymer/carbon.
Technical Approach

**Processing**
Processing the precursors (MPPO, MPEEK and PEI) at high melt shear rates further controls the morphology and orientation of crystalline regions.

**Hydrogen Storage (Physisorption & Chemisorption)** Prepare carbon and activated polymer – based carbons, determine the storage characteristic, pore size distribution, high ultramicropore volume and high ultramicroporosity prepared with various activation agents.

**Physisorption in carbon/polymer** Conduct H\(_2\), N\(_2\) and He adsorption measurements. Study and correlate surface area, ultramicropore volume, pore size distribution and storage to the methods of the carbon synthesis.

**Chemisorption** Study methods of incorporating reactive sites into the pores of activated carbon/polymer. Investigate organometallics, metal hydrides and multicyclic ligand- doped carbons.
Nanostructured Activated Polymer Carbon Preparation Methodology

**Polymer Precursor**

**Modification:**
- stabilization
- crosslinking

**Carbonized Polymer**

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

**Doped Carbon**

**Doping:**
- dopant - metal
- organometallics
- multicyclic ligands
- temperature

**Activated Carbon**

**Activation:**
- activation agent
- temperature
- homogeneity
Organometallic and Multicyclic Ligand Dopants

Metal center (Mg, Ti, Sc, Ru, Pt and other transition metals)

Monomeric and Polymeric Organometallic Dopants Screened by PM3 Computation
Correlation of Surface Area with Pore Size of Activated Polymer Carbons

Formation of porous structure

1\textsuperscript{st} Stage Burn-Off: pore creation dominates $\rightarrow$ higher surface area, smaller pores;

2\textsuperscript{nd} Stage Burn-Off: pore enlargement and fusion dominate $\rightarrow$ higher surface area, larger pores.

**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 $\sim 8 \text{ Å}$

All points represent experimental data
[CNH]_n doped high surface area polymer carbon

BET surface area: 1850 m²/g
Pore Vol.: 0.84 mL/g
Average Pore Width: 8.52 Å
**Strategy I**: Develop a set of activation agents. Activation agent MK has a better affinity to carbon matrix, allowing homogeneous activation and, hence, narrow pore size distribution.

**Strategy II**: Doping the activated carbon with polycyclic compounds to tailor pore size and distribution. Average pore size decreases from 18.6 Å for undoped carbon to 8.5 Å of [CNH]_n doped carbon.
Strategy III: Adjusting carbonization temperature. Carbonization at 600-800 °C achieves the desired pore diameter and surface area.

Strategy IV: Adjusting activation temperature to achieve the desired pore diameter and surface area.
Reproducibility of the Production of Activated Polymer Carbons

10-g batch synthesized carbons shows a variation of surface area ± 2.4% and hydrogen capacity ± 2.0% at 77 K and 1 bar.
Hydrogen sorption is reversible at 77 K and pressure up to 1 bar;
Gravimetric and volumetric capacity both increase as average pore size decreases from 22 to 17 Å. (All carbon samples shown in the figures have a similar BET surface area of ~ 2700 m²/g);
Small pore size is essential for high hydrogen storage capacity.
Correlation of Hydrogen Gravimetric Capacity With Specific Surface Area at 77 K and 1 Bar

Gravimetric capacity increases as surface area increases at ~19 μg H₂/(m²/g) below surface area of ~1800 m²/g;

Gravimetric capacity of ~ 3.0 wt% is achieved with surface area of ≥ 1800 m²/g at 77 K and 1 bar.
The influence of pore size on hydrogen gravimetric and volumetric capacity (77 K, 1 bar). Small pores increase hydrogen uptake density.
Excessive Hydrogen Uptake of Polymer Carbons at 77 K and High Pressure

- The gravimetric storage capacity recorded up to ~ 6.7 wt%;
- Carbon samples synthesized in this laboratory were sent to multiple institutions for high pressure hydrogen uptake. The data show measurement conducted by: *Gas Technology Institute, Inc., Université du Québec à Trois-Rivières and Oak Ridge National Laboratory.*

* MK775 measured up to 2 MPa due to instrument limitation.

At 77 K and 60 bar, experimental data shows that decreasing the pore size increases H$_2$ volumetric density.
Dependence of Maximum Hydrogen Uptake at 77 K on BET Surface Area

- Maximum hydrogen uptake increases linearly with surface area, at a rate of \( \approx 20 \ \mu g \) H\(_2\)/(m\(^2\)/g), which indicates \( \approx 6 \) H\(_2\) molecules occupy 20 graphene hexagon units. [Hirscher, et al., *Carbon* 2005, 43, 2209]

- A gravimetric capacity of up to 6.7 wt% has been achieved on a high surface area carbon (\( S_{\text{BET}} \approx 4000 \) m\(^2\)/g, pore vol \( \approx 2.30 \) mL/g).

- The circled sample has a microporosity of \( \approx 96\% \) with an average pore width of \( \approx 14.2 \) Å, and exhibits a volumetric capacity of up to 45 g H\(_2\)/L.
## Progress Project Summary

### Hydrogen Storage Capacity of Polymer-Derived Carbon Nanostructures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer</th>
<th>Porous Texture</th>
<th>H₂ Storage, 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$S_{BET}^a$ (m²/g)</td>
<td>Pore Vol. (mL/g)</td>
</tr>
<tr>
<td>MK725*</td>
<td>PEEK</td>
<td>1800</td>
<td>0.87 (0.84)</td>
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<tr>
<td>APKI11-4</td>
<td>PEEK/PEI</td>
<td>2110</td>
<td>1.03 (0.98)</td>
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<tr>
<td>APKI6S11</td>
<td>PEEK/PEI</td>
<td>2480</td>
<td>1.20 (1.14)</td>
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<tr>
<td>APK94-3</td>
<td>PEEK</td>
<td>2650</td>
<td>1.54 (1.32)</td>
</tr>
<tr>
<td>MK775</td>
<td>PEEK</td>
<td>2680</td>
<td>1.15 (1.10)</td>
</tr>
</tbody>
</table>

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<tr>
<td></td>
<td></td>
<td>$S_{BET}^a$ (m²/g)</td>
<td>Pore Vol. (mL/g)</td>
</tr>
<tr>
<td>APKI6S7</td>
<td>PEEK/PEI</td>
<td>3320</td>
<td>1.67 (1.49)</td>
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<tr>
<td>APKI6SN3</td>
<td>PEEK/PEI</td>
<td>3300</td>
<td>1.85 (1.47)</td>
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<tr>
<td>APO60S-R10</td>
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<td>3920</td>
<td>2.20 (1.72)</td>
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<tr>
<td>APKI6SN5</td>
<td>PEEK/PEI</td>
<td>4020</td>
<td>2.30 (1.75)</td>
</tr>
</tbody>
</table>
Demonstrated synthesis of carbons with high surface area (up to 4000 m$^2$/g) and low average pore width (down to 8.5 Å);

Accomplished gravimetric storage capacity of ~ 6.7 wt%, and volumetric capacity of ~ 45 g/L at 77 K, 5 - 6 MPa.

Formulated synthetic strategies toward polymer-based nanostructured carbons of controllable porosity and surface area;

Achieved reproducibility (>98% in terms of surface area and pore volume) in 10-gram scale batch production of high surface area carbon;

Enabled carbon doping with organometallic compounds that exhibit rigid planar configuration and are rich in electronegative nitrogen atoms, $[CNH]_n$, may enable application for RT and moderate pressure H$_2$ storage system;

Established correlation of hydrogen storage with surface area, pore size and porosity;

Demonstrated hydrogen storage capacity of up to ~3.0 wt% at 77 K and 1 bar.
Planned work for FY08-FY09:

- Continue to develop, modify, characterize and scale-up produce nanoporous polymer materials and carbons.
- Continue to develop methods of doping polymer – blend / carbon with metal hydrides (e.g., MgH$_2$ and RSiH$_n$), organometallic and multicyclic ligand compounds.
- Increase hydrogen binding energy by surface modification and doping with heterocyclic and heteroaromatic polymers.
- Characterization of doped activated carbons and hydrogen storage capacity evaluation.
- Elevated temperature hydrogen adsorption tests of organometallic-doped PEEK carbons.