# Polymer-Based Activated Carbon Nanostructures for $H_2$ Storage

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

- High BET surface area > 2600 $m^2/g$;
- High microporosity > 95%;
- Average pore size ~ 10 Å;
- Hydrogen uptake: ~ 5 wt% and 40 $gH_2/L$ 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 - June 2010
- 75% 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 2009
  - $250K
- Funding for FY 2010
  - no money received

## Barriers

- Improved gravimetric and volumetric density of $H_2$ uptake
- Controlled matrix doping and polymers compatibility
- Improved heat $H_2$ of adsorption

## Partners

***PoroGen (Boston MA)-*** *on polymer blend development and precursors*

***collaborations:***

***-GTI (Chicago) High pressure testing***

***-HidenIsochema Co. UK high pressure testing and evaluation***

***Also***

***- Quantachrome Ins. Surface structure***

***- NiMO electrical***

***-OAK Ridge NL***

***-Lawrence Berkeley NL***

# 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.

| Performance Measure | June, 2009 – May, 2010 performance Target |
|---|---|
| **Carbon Surface Area and Pore Volume** | **$S_{BET}$ > 3000 $m^2$/g**<br>**$V_{mp}$ > 1.4 cc/g** |
| **Hydrogen Storage Capacity** | **Gravimetric Capacity (Material Based) >6 wt%**<br>**Volumetric Capacity (Material Based) >40 g/L** |
| **Durability of Hydrogen Storage on Carbon** | **> 30 cycle** |
| **Incorporation of Unsaturated Functionalized Polycyclic Complexes (Melem, F-Melem, Ni-Melem)** | **> 20 wt% on Carbon** |
| **Improve Hydrogen Binding Energy** | **>>12 kJ/mole** |

# Technical Approach

## Task 1: Processing Precursors

95 % complete

- Material Development
- Modification
- Characterization

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

## Task 2: Nanostructured Carbon Preparation

80 % complete

- Prepare high surface area activated polymer based carbon
- Analysis morphology (surface area, porosity, pore volume and size distribution)
- Production scale up

## Task 3:Hydrogen Storage (Physisorption &Chemisorptions)

70 % complete

Incorporating reactive sites into the carbon nanostructures.

Incorporation and polymerization of unsaturated functionalized polycyclic complexes (Melem, F-Melem, Ti,Fe Mg V N iMelem) 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 other M).

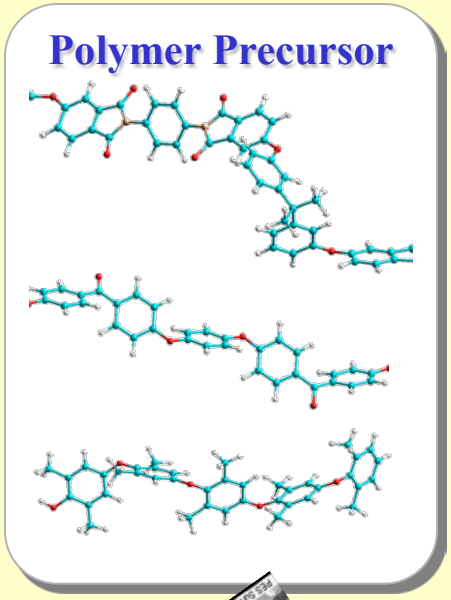
## Task 4: Hydrogen Storage Testing

60 % complete

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

**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

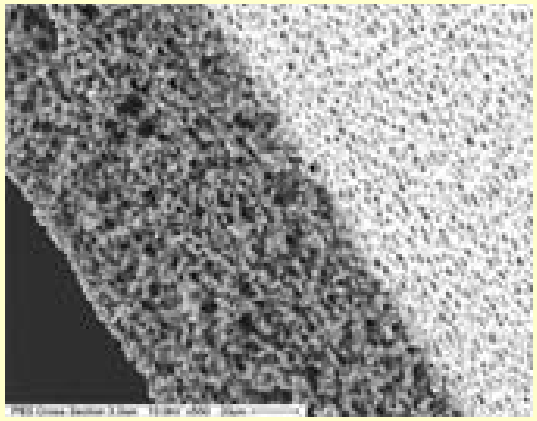



1.modification
2.processing

PEEK

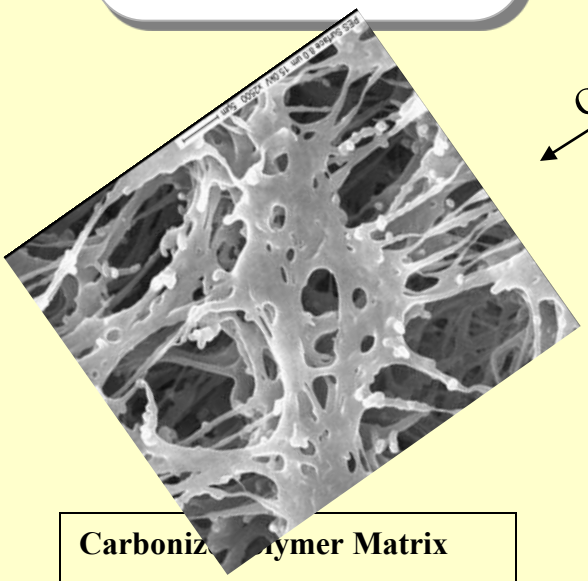
PEEK/PEI,

PPO



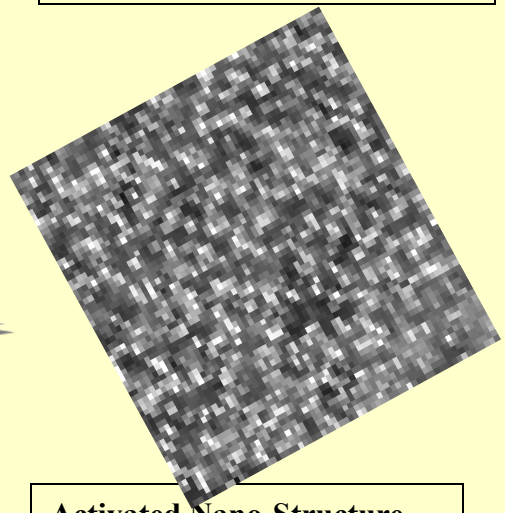
**Processed Polymer Matrix (highly porous medium)**

Carbonization



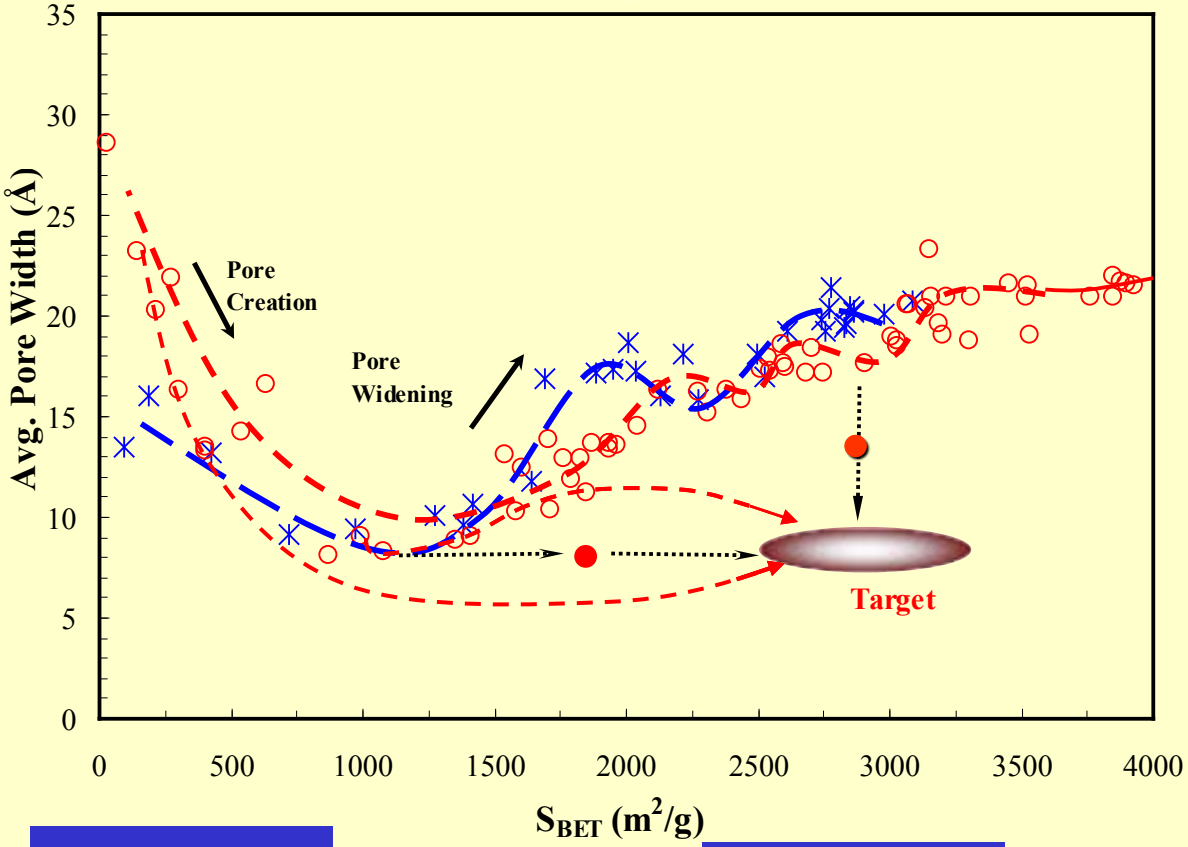
**Carboniz[illegible]ymer Matrix**

Activation



**Activated Nano-Structure Carbon Matrix**

# Correlation of Surface Area with Pore Size of Activated Polymer Carbons



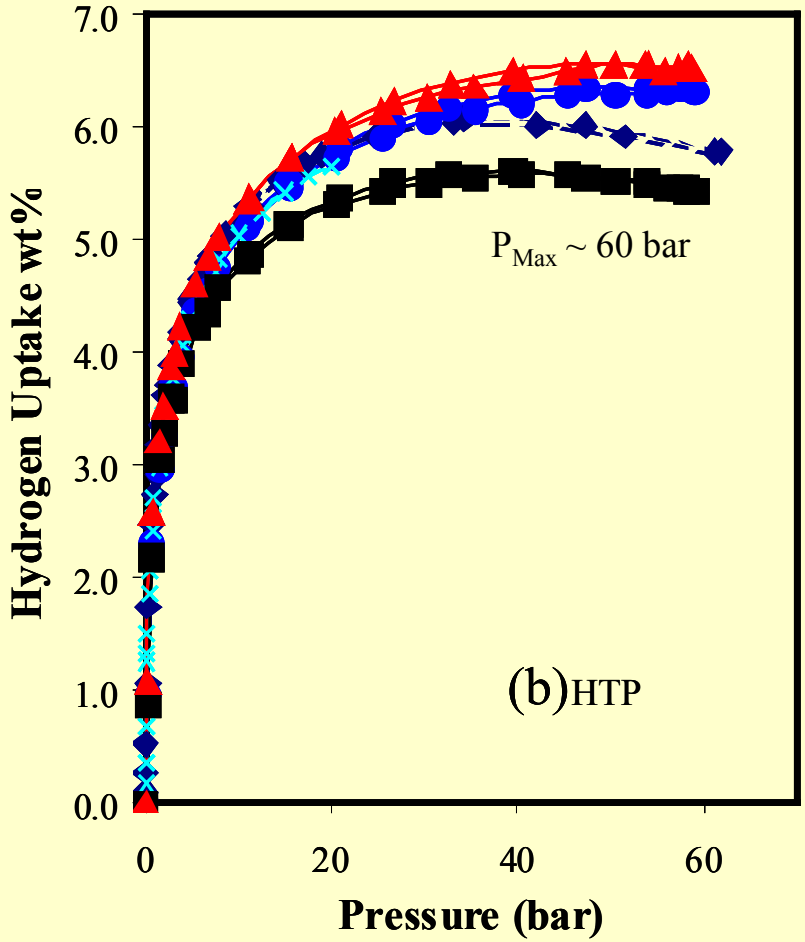

**Target:**

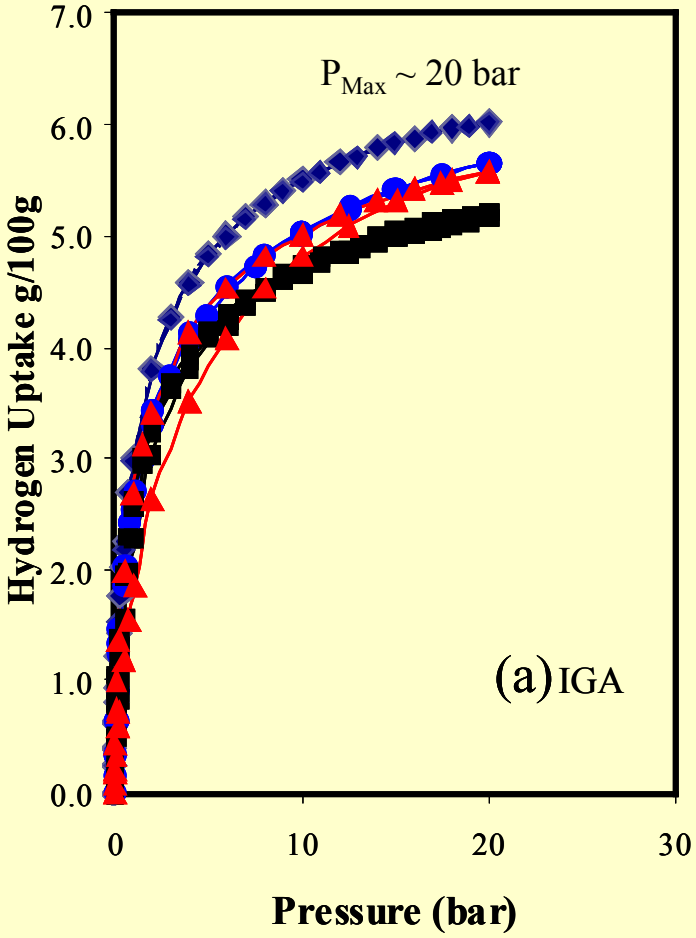
$S_{BET}$ > 2600 $m^2$/g with average pore width ~ 8 Å

**Achieved (●):**

$S_{BET}$ ~ 1850 $m^2$/g with average pore width ~ 8 Å

$S_{BET}$ ~ 2800 $m^2$/g with average pore width ~ 14 Å



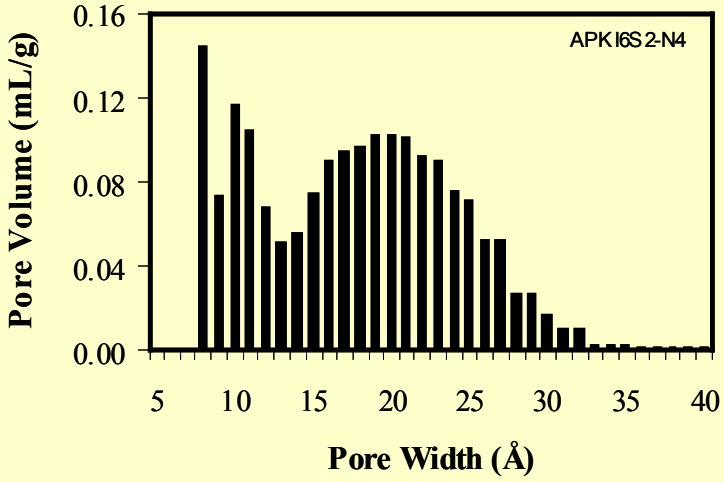



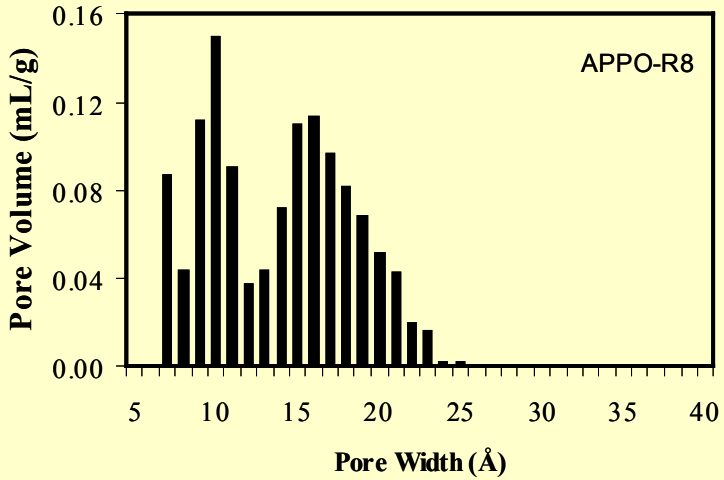

**Hydrogen Uptake isotherms** (excessive uptake) of polymer based carbons measured gravimetrically IGA (pressure up to 20 bar), and volumetrically HTP (instrument pressure up to 60 bar). The hydrogen uptake reaches 6.6 wt% for APKI-S6 at 50 bar, and for carbon 5.5 wt% 20 bar (as measured with both technique).

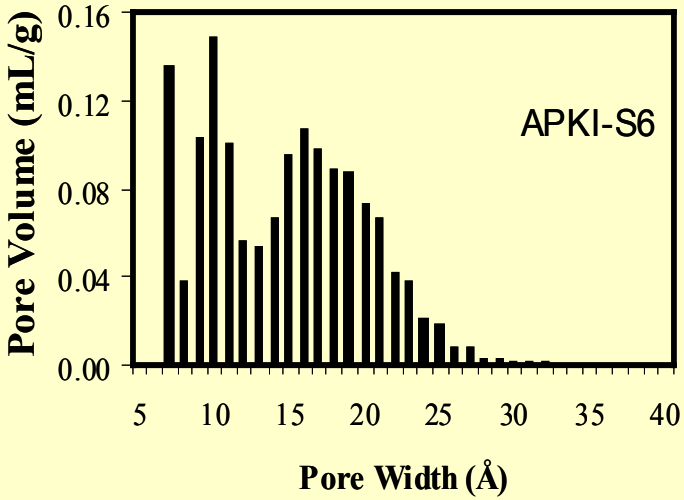
APKI6S2-N20 (♦), APKI6S-N4 (●), APKI-S6 (▲), APPO-R8(■). The APKI polymer-carbons are PEEK/PEI, and APPO is derivative of PPO.

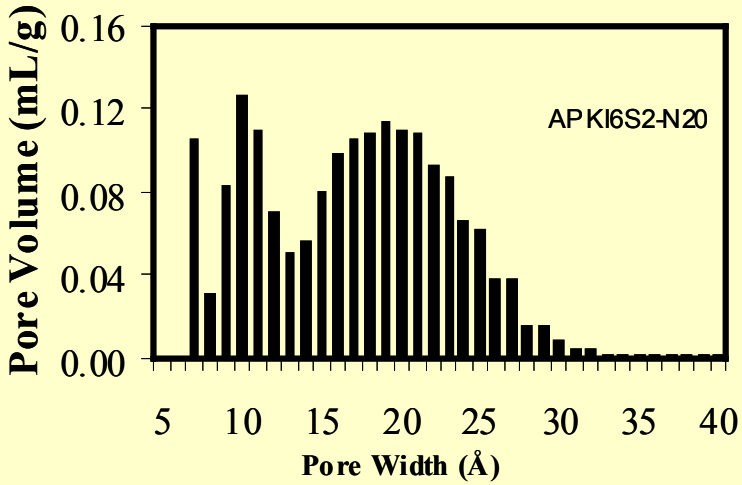


*Measurements done at HidenIsochema Co. U.K*

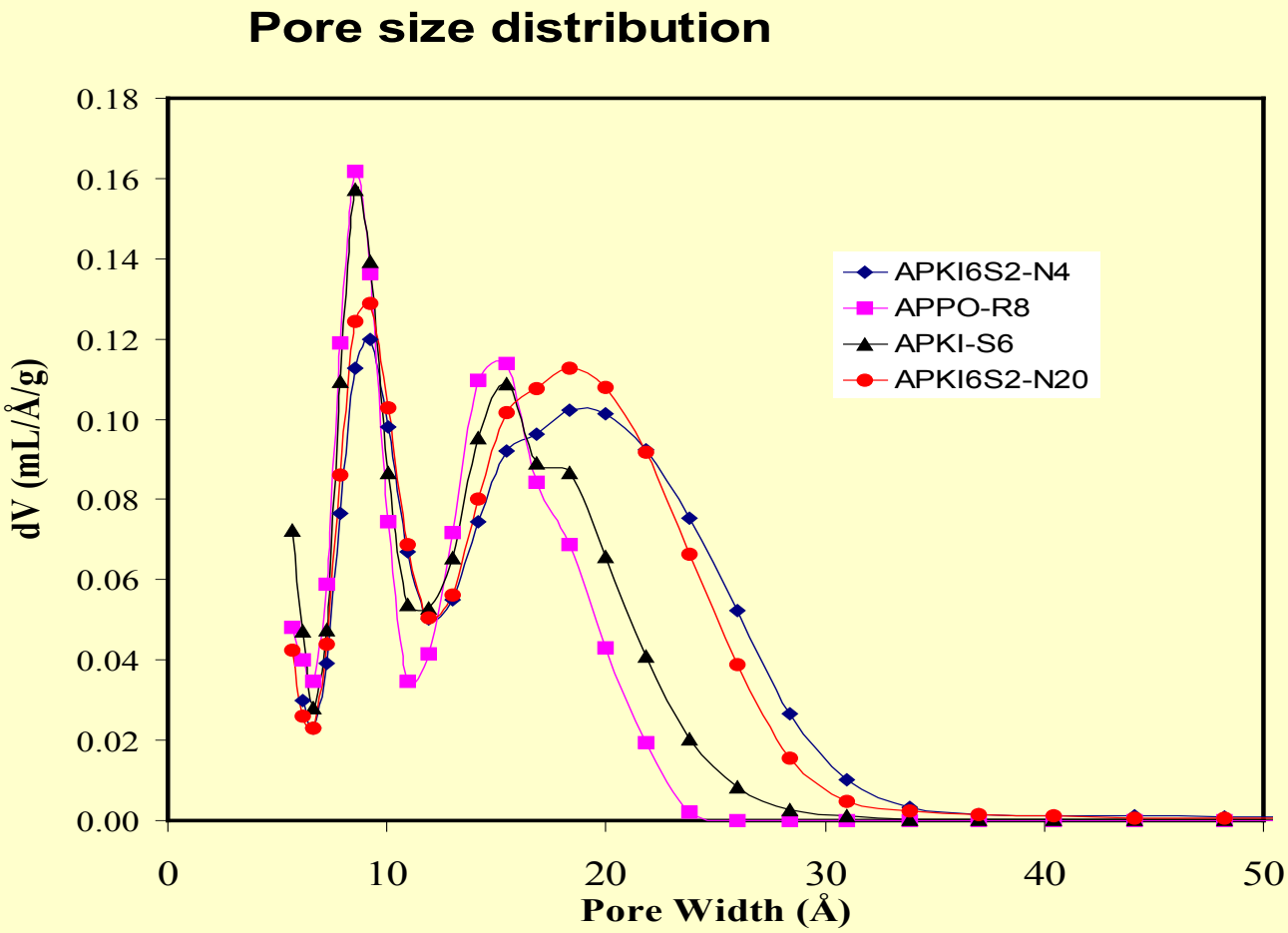


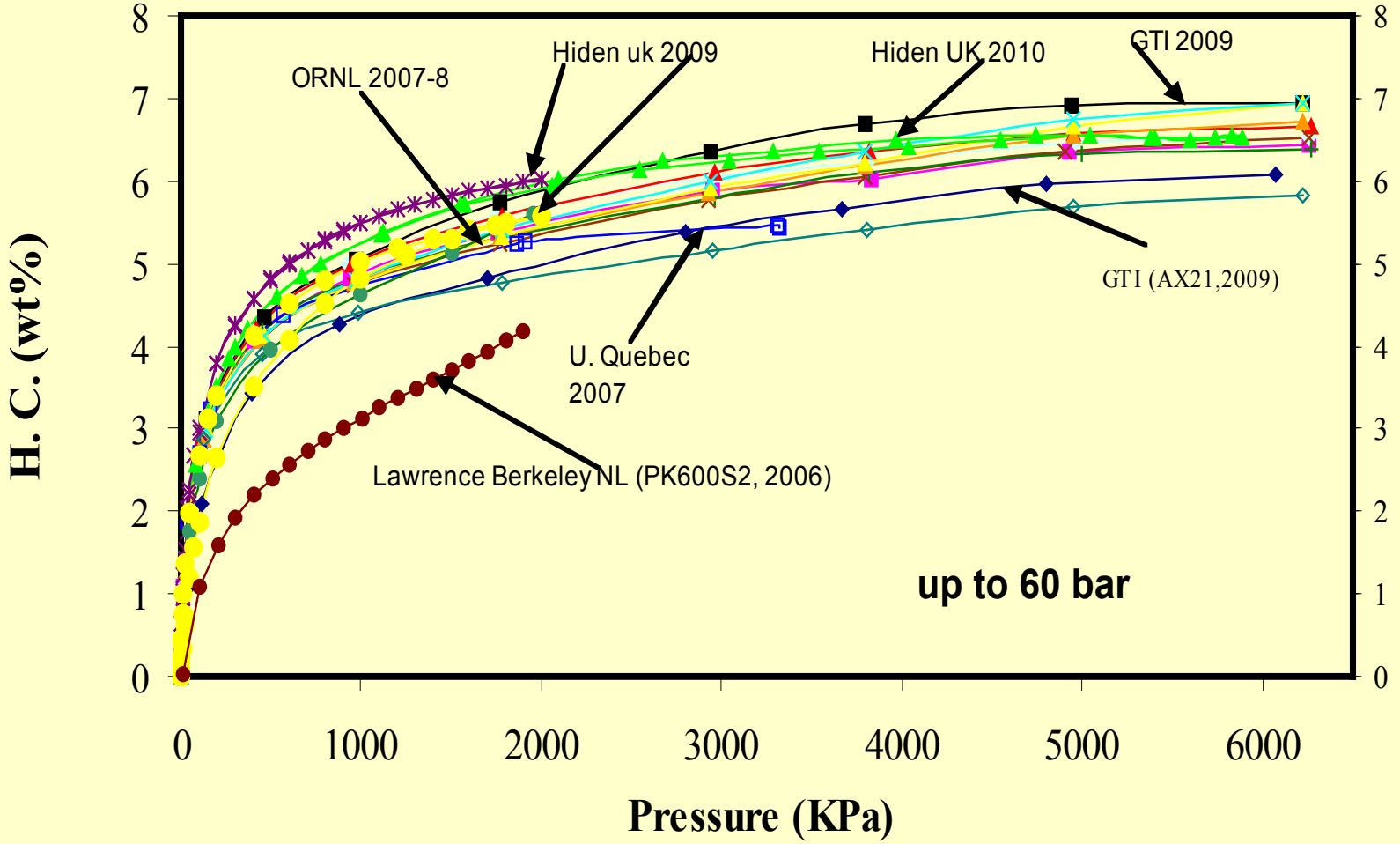




**Histogram plots (by QDFT calculation) of pore size distribution of polymer based carbon shown in previous slide.** (Surface areas for: APKI6S2-N4, APPO-R8, APKI-S6 and APKI6S2-N20 are recorded as 3070, 2550, 3034, 3160 $m^2/g$, respectively.)



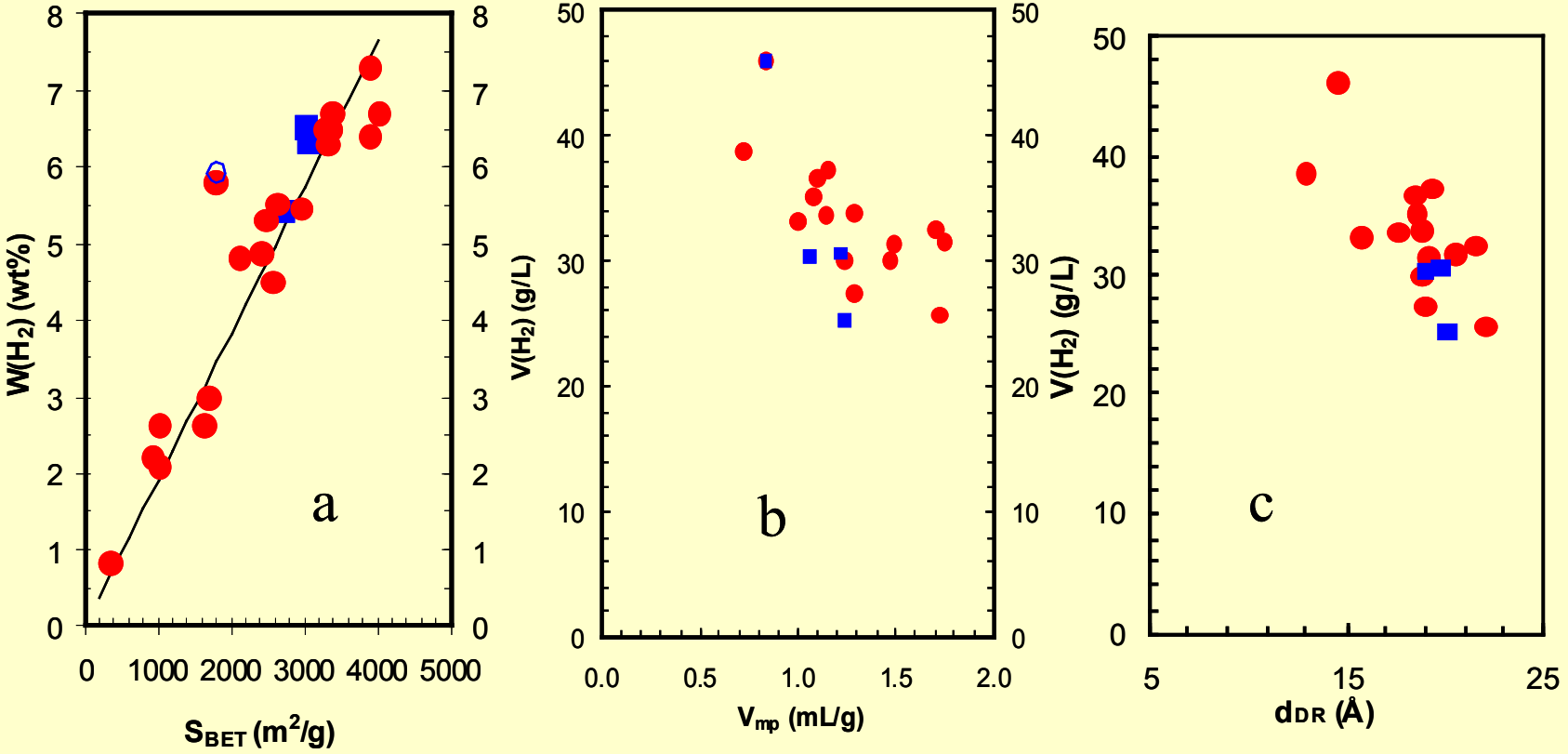

**Pore size distribution** calculated by QDFT method from N2 adsorption isotherms at 77K. (■) APPO-R8 (●) APKI6S2-N20 (♦), APKI6S2-N4, (▲) APKI-S6.

# Excessive Gravimetric Hydrogen Uptake Isotherms




**Excessive hydrogen uptake of polymer based carbons (PEEK, PEEK/PEI and APPO) at higher pressures. (evaluated at different testing laboratories).**

# Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures




- **a**. Gravimetric hydrogen uptake increases linearly with surface area, at a rate of ~ 20 μg $H_2/(m^2/g)$, which indicates ~ 6 $H_2$ molecules occupy 20 graphene hexagon units.
- **b**-**c.** High volumetric hydrogen uptake (up to 46 g $H_2$/L) is achieved at $V_{mp}$ ~ 0.8-0.9 mL/g.

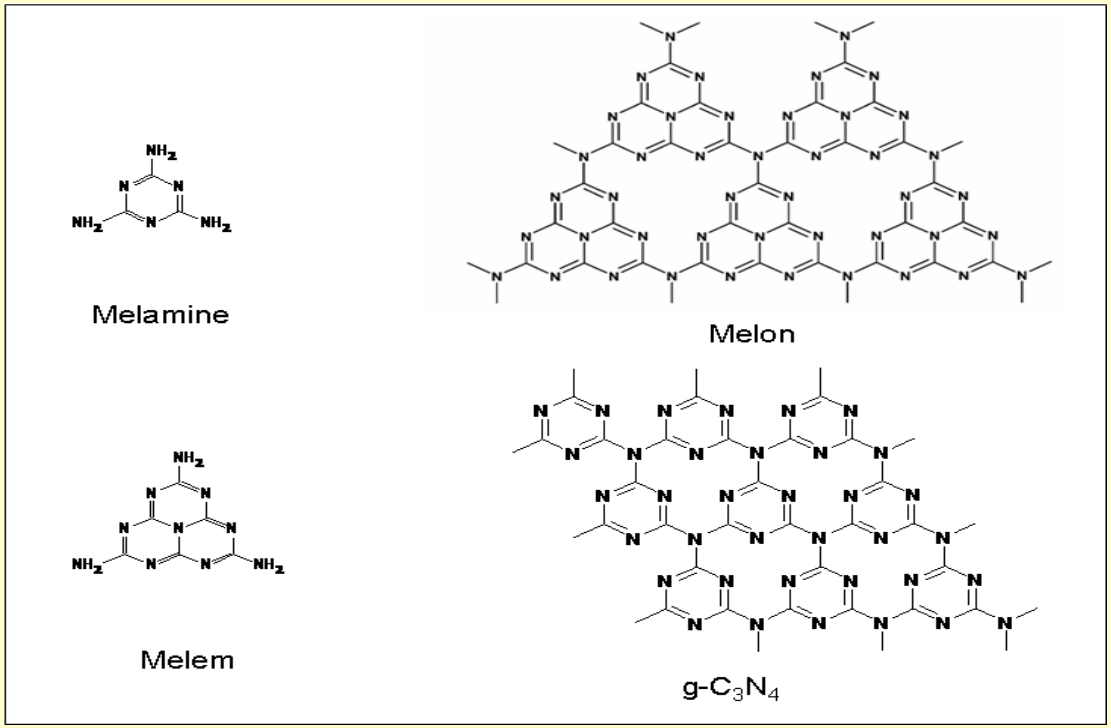
## Porous Texture and Hydrogen Storage Capacity of Polymer-Based Activated Carbon

| *Sample* | $S_{BET}$ $m^2/g$ | $V_{pore}$ $mL/g$ | $V_{mp}$ $mL/g$ | $d_{DR}$ Å | $\rho_a$ $g/mL$ | $W(H_2)$ ,wt% | | $V(H_2)$ , g $H_2/L$ | | $E_{ad}$ kJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 77 K, 60 bar | 298 K, 60 bar | 77 K, 60 bar | 298 K, 60 bar | |
| MK725 | 1800 | 0.870 | 0.840 | 14.6 | 0.749 | 5.8 | 0.80 | 46.1 | 6.4 | -5.2 |
| PKMNa | 1765 | 0.743 | 0.717 | 12.9 | 0.828 | 4.5 | 0.47 | 38.7 | 3.9 | -5.4 |
| MPK-3 | 2000 | 0.90 | 0.88 | 14.5 | 0.740 | 4.4 | N/A | 32 | N/A | -5.2 |
| MK750P | 2440 | 1.072 | 1.003 | 15.8 | 0.651 | 4.9 | 0.41 | 33.2 | 2.7 | -5.2 |
| APK6S11 | 2480 | 1.200 | 1.140 | 17.6 | 0.601 | 5.3 | 0.40 | 33.6 | 2.5 | -5.4 |
| PKMK_Bulk | 2490 | 1.077 | 1.077 | 18.6 | 0.648 | 5.1 | 0.59 | 35.1 | 3.8 | -5.2 |
| APOR8 | 2550 | 1.260 | 1.150 | 19.4 | 0.580 | 6.0 (5.5) | 0.50 | 37.3 | 2.9 | -5.2 |
| PK775C | 2680 | 1.150 | 1.100 | 18.5 | 0.619 | 5.6* | N/A | 36.7* | N/A | -5.2 |
| APKIS13 | 3025 | 1.380 | 1.290 | 18.8 | 0.542 | 5.9 | 0.48 | 33.8 | 2.6 | -5.1 |
| APKi6S7 | 3320 | 1.670 | 1.490 | 19.1 | 0.468 | 6.3 | 0.50 | 31.5 | 2.5 | -5.2 |
| APO-R10 | 3100 | 2.200 | 1.720 | 22.1 | 0.375 | 6.4 | 0.50 | 25.7 | 2.0 | -4.9 |
| APKi6SN3 | 3300 | 1.850 | 1.470 | 18.8 | 0.432 | 6.5 | 0.45 | 30.0 | 2.1 | -5.2 |
| APKi6SN5 | 3070 | 1.810 | 1.230 | 20.6 | 0.440 | 6.7 | 0.59 | 31.6 | 2.8 | -5.1 |
| APKI6S-N20 | 3070 | 1.990 | 1.240 | 21.6 | 0.407 | 6.8(6.0) | 0.50 | 32.5 | 2.0 | -5.3 |
| APKI6S2-N4 | 3073 | 1.997 | 1.240 | 21.6 | 0.500 | 6.9(6.3) | N/A | 25 | N/A | -6.0 |
| APKI-S6 | 3034 | 1.63 | 1.240 | 18.0 | 0.475 | (6.5) | N/A | 31 | N/A | -5.5 |

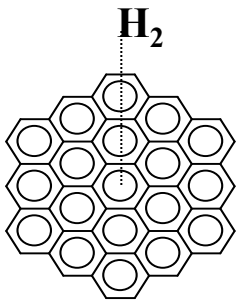
- Measured at 77 K and 20 bar.
- The values in the parenthesis measured by Hidenisochema Co.

- 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.

# Introduction of a carbon alloyed with organo*cyclic-CNH$_n$ macromolecules*



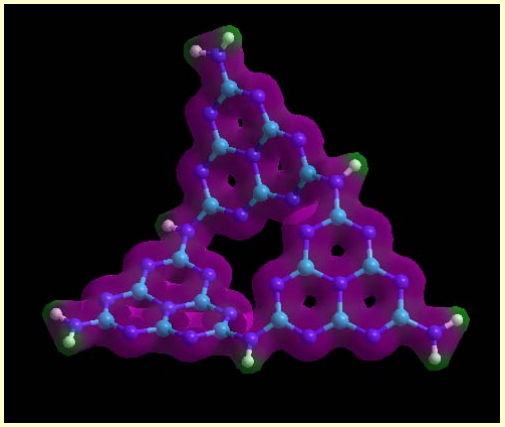

**Interaction of carbon with hydrogen is relatively low (see scheme) and may reach up to 6-7 kJ/mol . Introduction of a carbon alloy with organo*cyclic-CNH$_n$ macromolecules*** *rich with unsaturated bonds (*that exhibit rigid planar configuration and are abound in electronegative nitrogen atoms) can complex metal-salt and are enable for RT application for $H_2$ storage systems in moderate pressure. (note, the interaction with cyclic bonds can reach 80-100 kJ/mol, thus control and monitor the interaction binding energy in of concern to $H_2$ storage work is in progress).



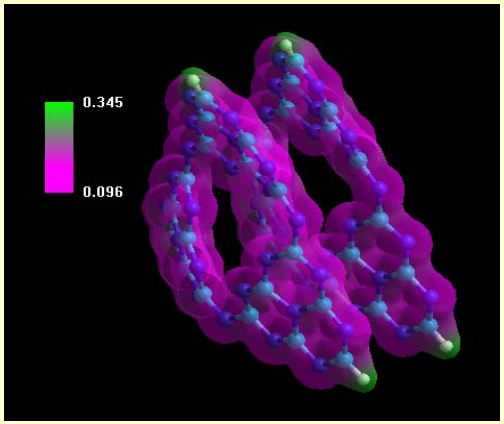

The potential minima of between $H_2$ and 19 benzene rings is –3.6 kJ/mol

Melamine derivatives have been synthesized and carbonized are incorporated into activated carbon 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.

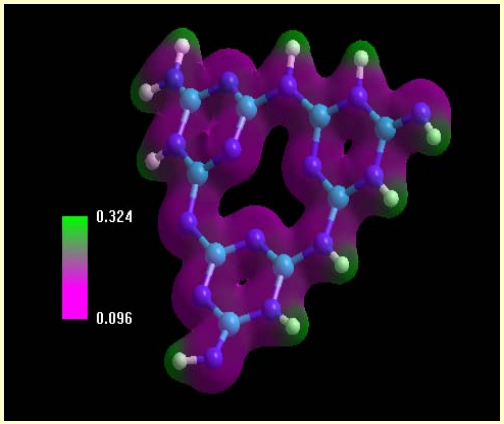
# Monte Carlo Computing and 3D Mapping Iso-Surface of Melem Configuration



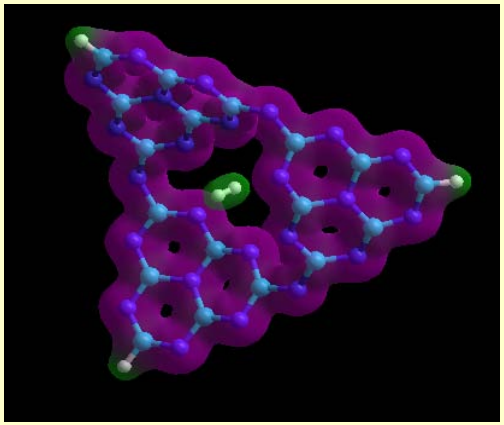
Melon



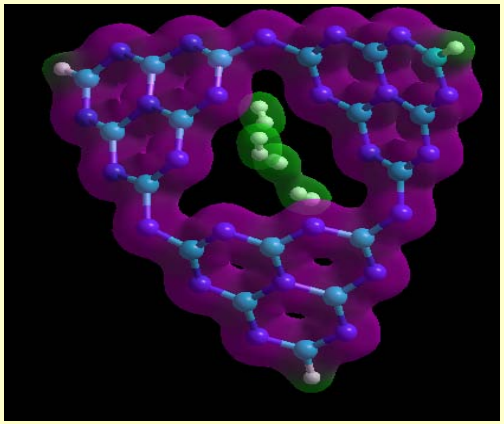

Melon




g-C3N4



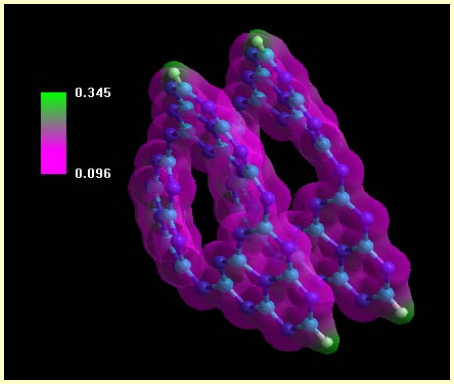
Melon –1H



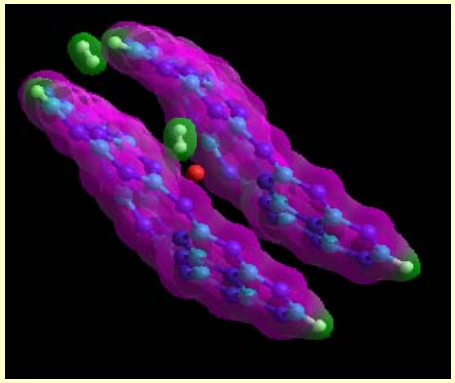
Melon-4H

**Monte Carlo computation of electro-charge density and 3D mapping iso-surfaces of melon at 300 $^{o}$K**. The electro-charge density from positive to negative is shown as green to purple. Above are shown the basic unit cell of Melon and g-C3N4; below, $H_2$ adsorbed on Melon.

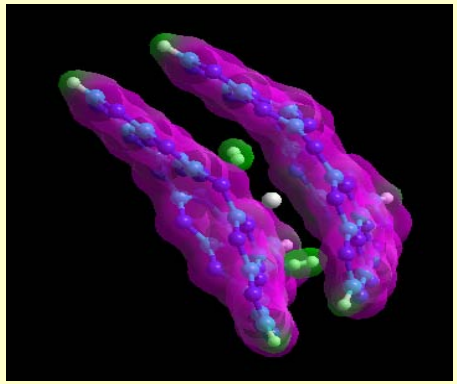
**Monte Carlo Compute and 3D Mapping Iso-surface of Melon and Complex with Metal Atoms Configuration**



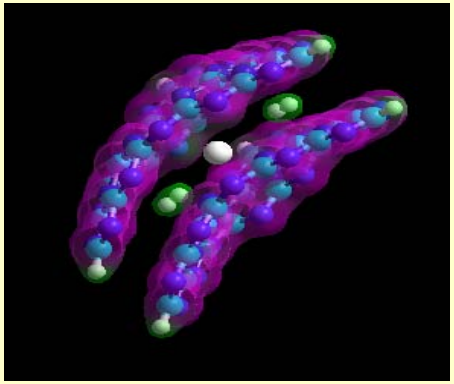

2Melon d=3.4 A



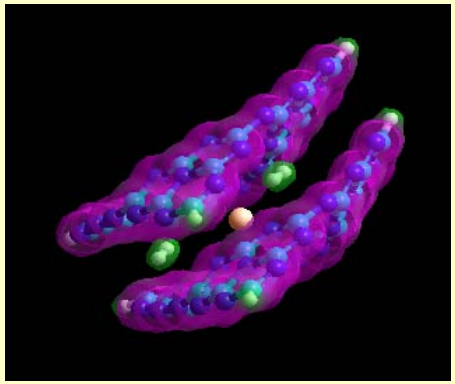
2Melon –Fe-2H.d=3.68 A



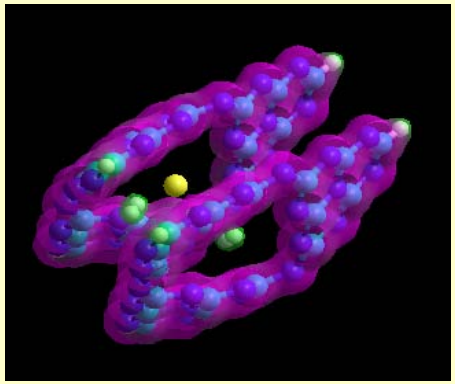
2Melon –V-2H.d=3.93 A



2Melon –Ti-2H.d= 4.5 A

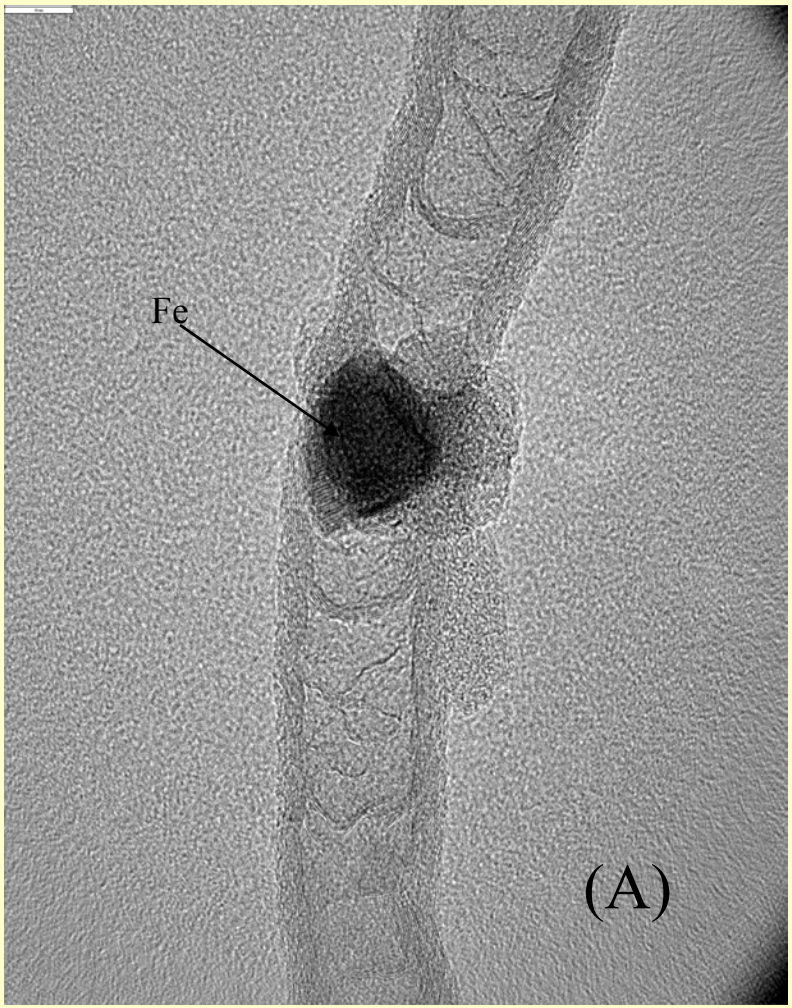


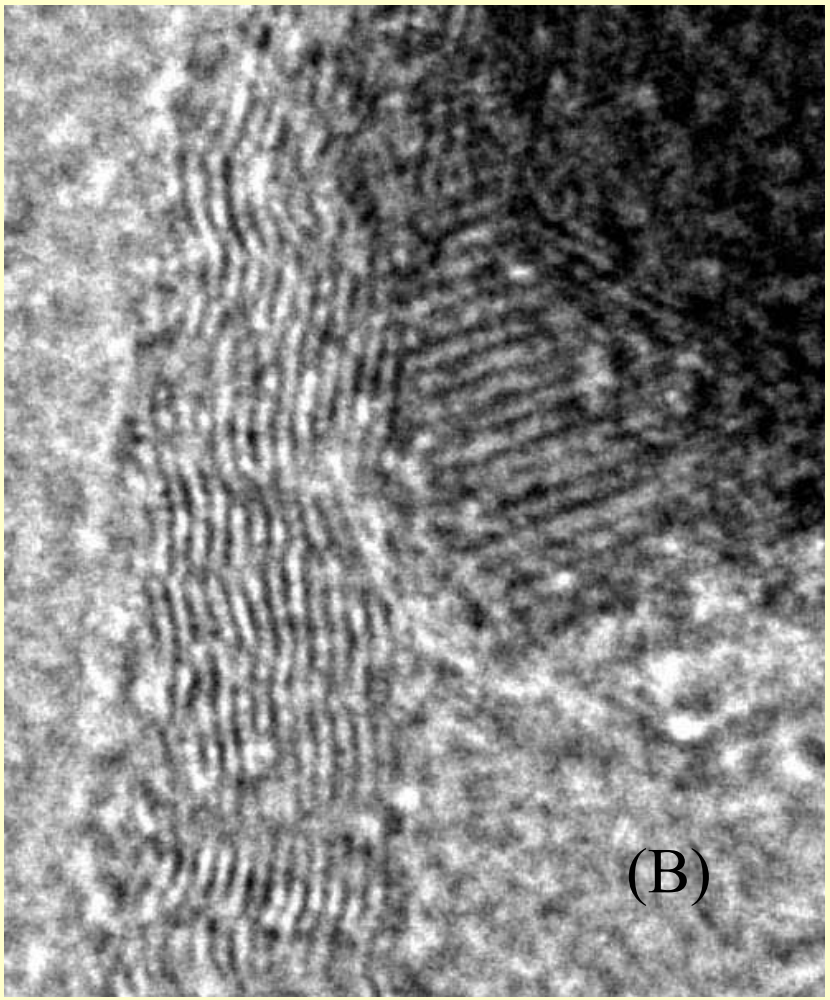
2Melon –Mg-2H.d=4.24 A



2Melon –Ni-2H.d=3.43 A

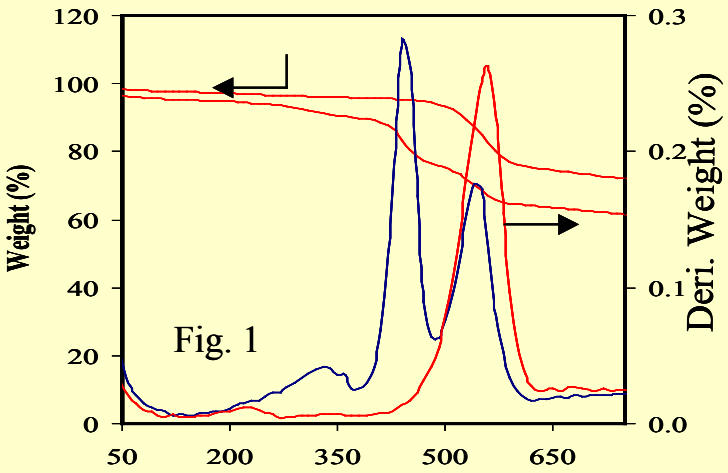
**3D mapping iso-surfaces of two parallel unit Melon configuration at 300 $^{o}$K**. 2 $H_2$ adsorbed with Mg, Fe, Ti, V, Ni single metal atoms. The electro-charge density from positive to negative is shown from green to purple. These models indicate that Ti and Mg do not only interact with the melon units but also "open" the spacing for hydrogen (up to four for Ti and two for Mg) which were situated here at the local 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.

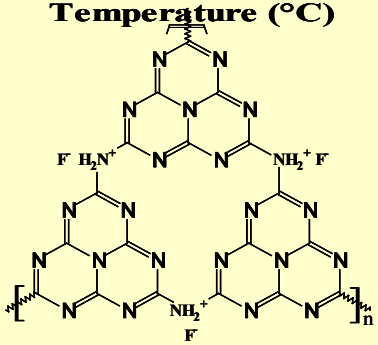


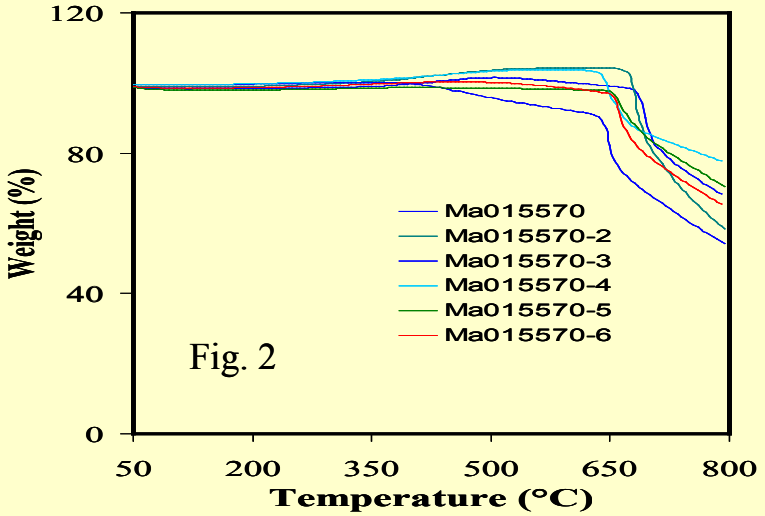

**TEM image of carbonized Melon**. The melon carbonized at 700$^{o}$ C form C-N nano tubing with diameter ~12 nm . Right image shows lattice structure formed on wall of this carbon. The electro diffraction gives distance of 3.4 Å. Traces of large cluster aggregation of **Fe** is sown in (A).

# Characterization of Melem Derivatives

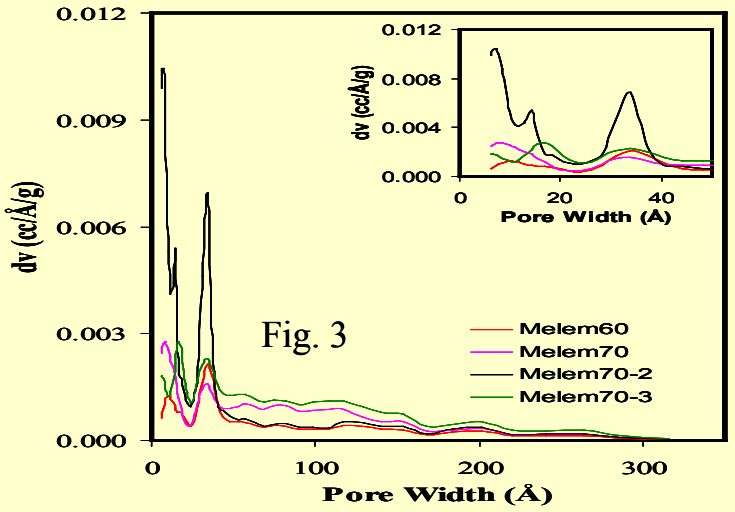


The thermal behaviour of the ([C-N-H]n+)nF-n on the carbon was investigated and shown in Figure 1. The TGA of CNH doped carbon shows single stage decomposition, with weight loss at 560°C. However, ([C-N-H]n+)nF-n doped carbon shows a mutil-stage partial degradation at 300°C, 440°C and 560°C.

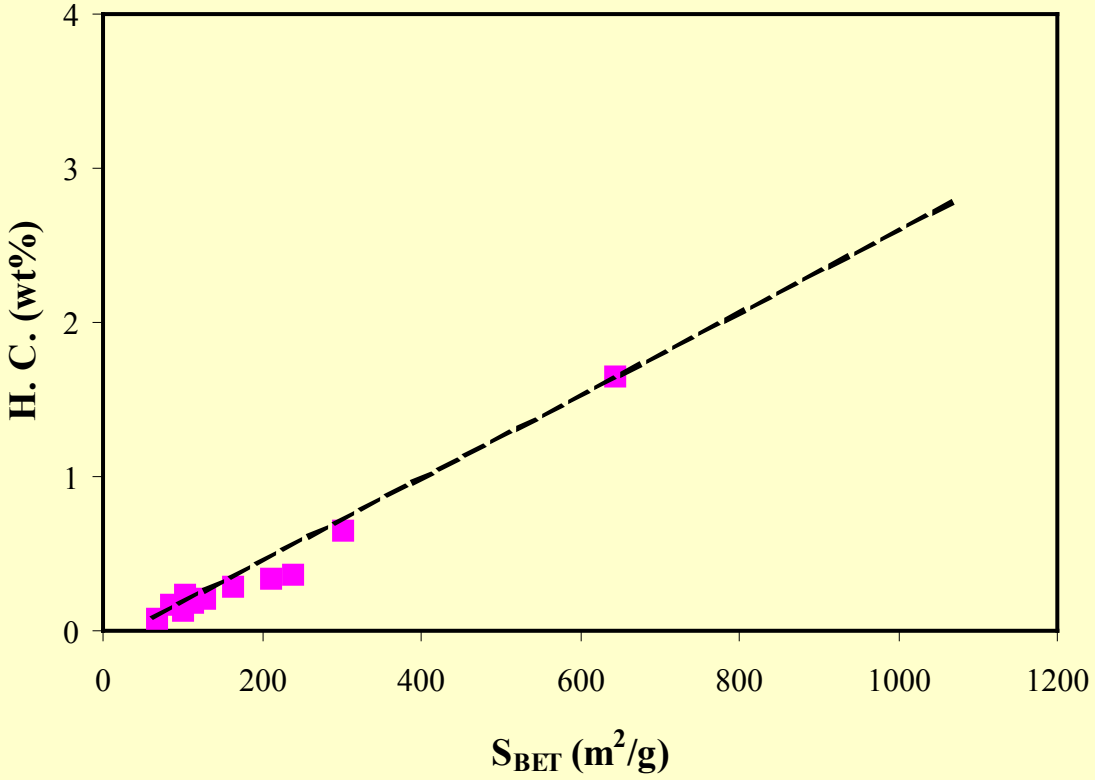



The decomposition behaviors of carbonized melem samples. All the samples have a transition temperature start ~ 650°C



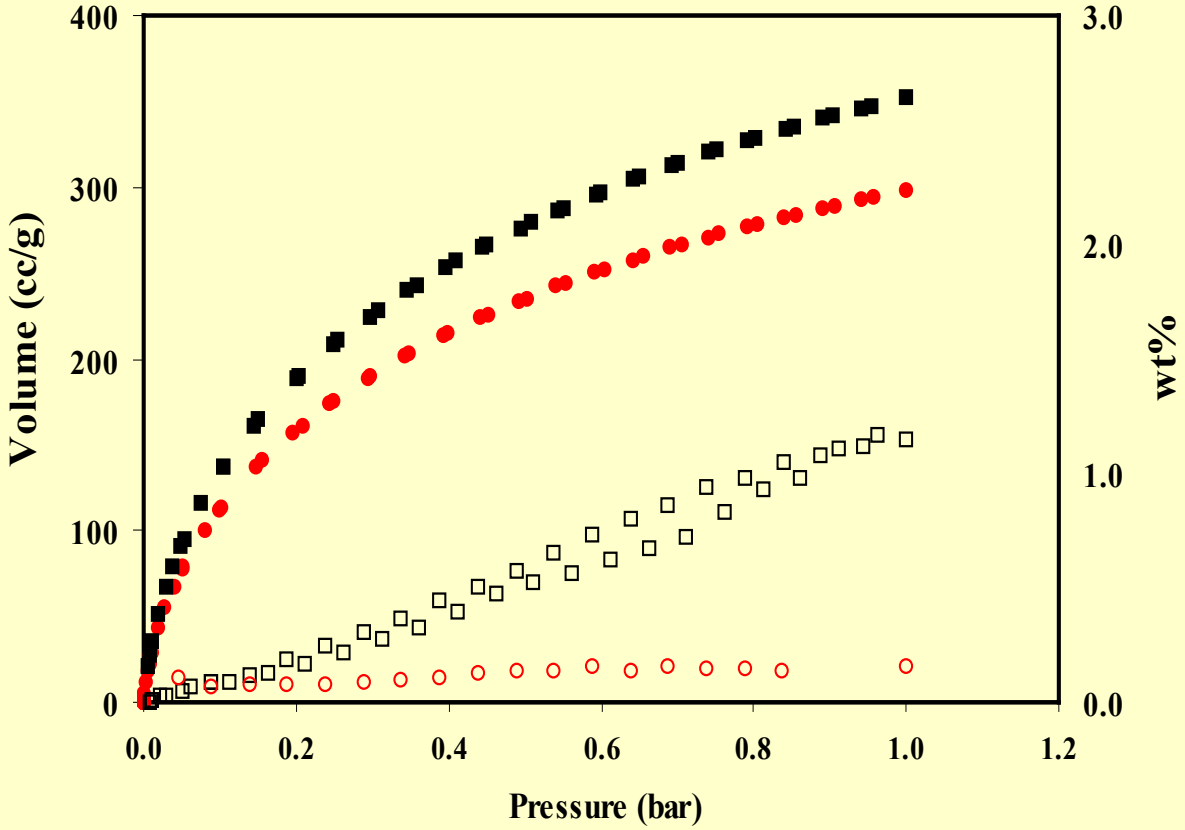

Pore Size Distribution of Carbonized Melon

# Hydrogen storage Capacity at 77K 1bar of Melem Based Carbons




**Hydrogen adsorption of carbonized Melon before complex with Metal at 87 $^0$K and 1 bar**. All the samples have surface area below 650 $m^2$/g. The hydrogen adsorption increase linearly with the surface area. (uptake about ~3 wt% hydrogen can be obtained by extrapolating to the surface area ~ 1000 $m^2$/g.)

# Hydrogen Adsorption Isotherms of PZT Doped Carbon




PZT ~20Å size (Pb-Zr-Ti) was synthesized and incorporated into a high surface area carbon. Hydrogen storage capacity of PZT/carbon is shown to have higher value than non doped carbon. (PEEK- carbon $S_{BET}$ ~2890 m2/g, *dDR* ~18.5 Å)

PZT 77K(■), 273 K (□) and carbon at 77 K (●), 273 K (○).

# Project Summary

***The data shown and presented in these slides represents part of activity of the project this year.***

**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 $m^2/g$) 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 organo*cyclic-*$CNH_n$ *macromolecules** *rich with unsaturated bonds* that should be available 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 77K and 1 bar is 4-5 wt% with surface area ~2000 $m^2/g$.

----------**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.

**This study is in progress.**

# Future work

**We concur that the carbon matrix by itself has a slim chance (if at all) to produce of interaction of about 20-25 kJ/mol needed for an effective adsorption 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 Metal-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.
- Theoretical simulations of hydrogen binding and adsorption.

**Supplemental slide**

# Collaborations

***PoroGen (Boston MA)- on polymer blend development and precursors and Technology Transfer***

**-GTI (*Chicago) High pressure testing***
***-HidenIsochema Co. UK high pressure testing and evaluation***

***<u>Also</u>***
***- Quantachrome Ins. Surface structure***
***- NiMO electrical and tech. transfer***
***-OAK Ridge NL testing***
***-Lawrence  Berkeley NL testing***

**Supplemental slide**

## Hydrogen Sorption Kinetic Profiles for Polymer Based Carbon