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:

Storage parameter	Unit	2015 System Target	SUNY-Syracuse
System Gravimetric Capacity	**KWh/kg (wy%H_2)**	**1.8 (5.5 wt%)**	**2.4(7.2)**
System Volumetric Capacity	**KWh/L(gH_2/L system**	**1.3 (40)**	**1.2 (38)**
Min/Max Delivery Temperature	**K**	**233-358**	**77**
Max Delivery Pressure	**Bar**	**100**	**60**

Overview

Timeline

- **Start - May 2005**
- **End - Dec. 2011**
- **75% Completed (due to DOE's budget shortage)**

Budget

- **Total project funding**
  - **DOE - $1.330K**
  - **Cost Share: $ (20%)**
- **Total funding obligated in FY 2010**
  - **$ 250K**
- **Funding for FY 2011**
  - **no funding planned**

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

Technical Approach

Task 1: Processing Precursors

95 % complete

- Material Development
- Modification
- Characterization

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

Task 2: Nanostructured Carbon Preparation

90 % complete

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

Task 3:Hydrogen Storage (Physisorption &Chemisorptions)

80 % complete

Incorporating reactive sites into the carbon nanostructures.

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

Task 4: Hydrogen Storage Testing

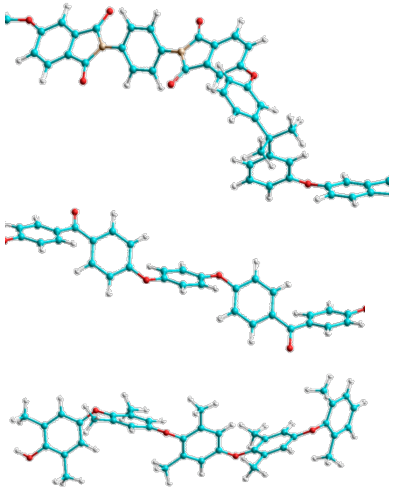
70 % complete

- 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

Polymer Precursor



1.modification
2.processing

Aromatic-based polymer

Process
Polymer Matrix
(highly porous
medium)

Carbonization

Carbonization with metal ion or CNH cyclic

Carbonize Polymer Matrix

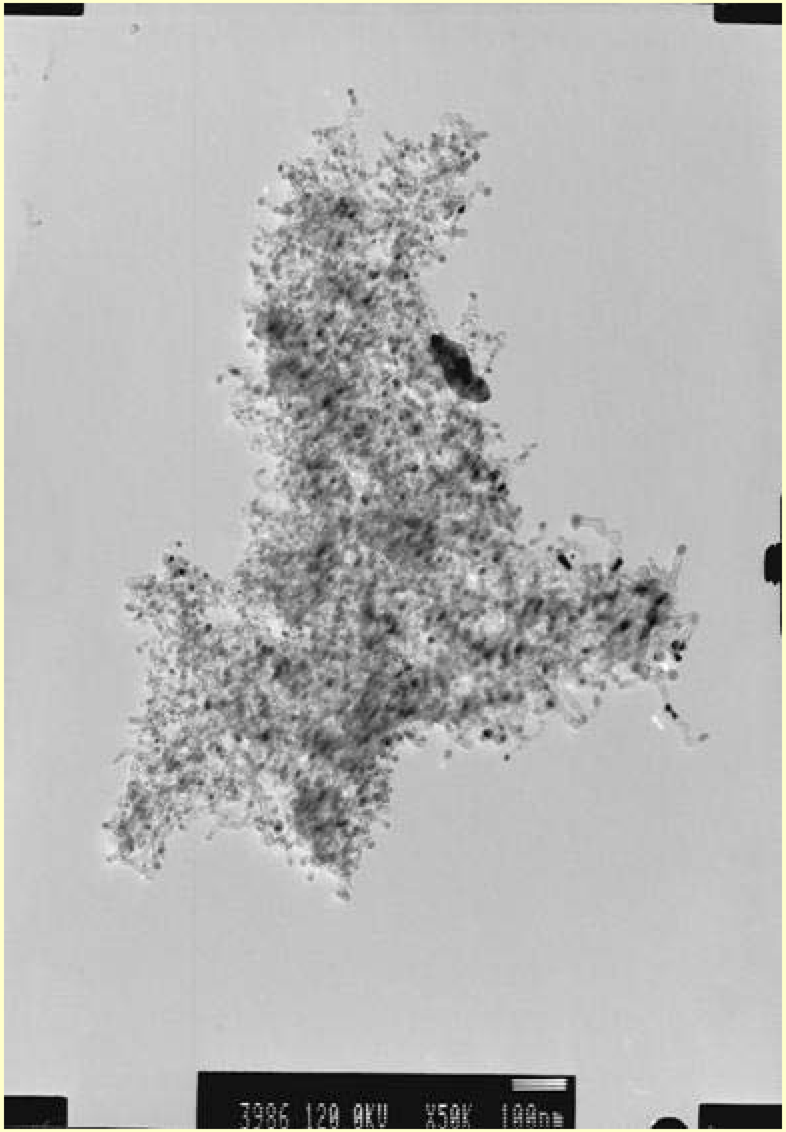
Carbonize Polymer doped with CNH,and metals

Activation

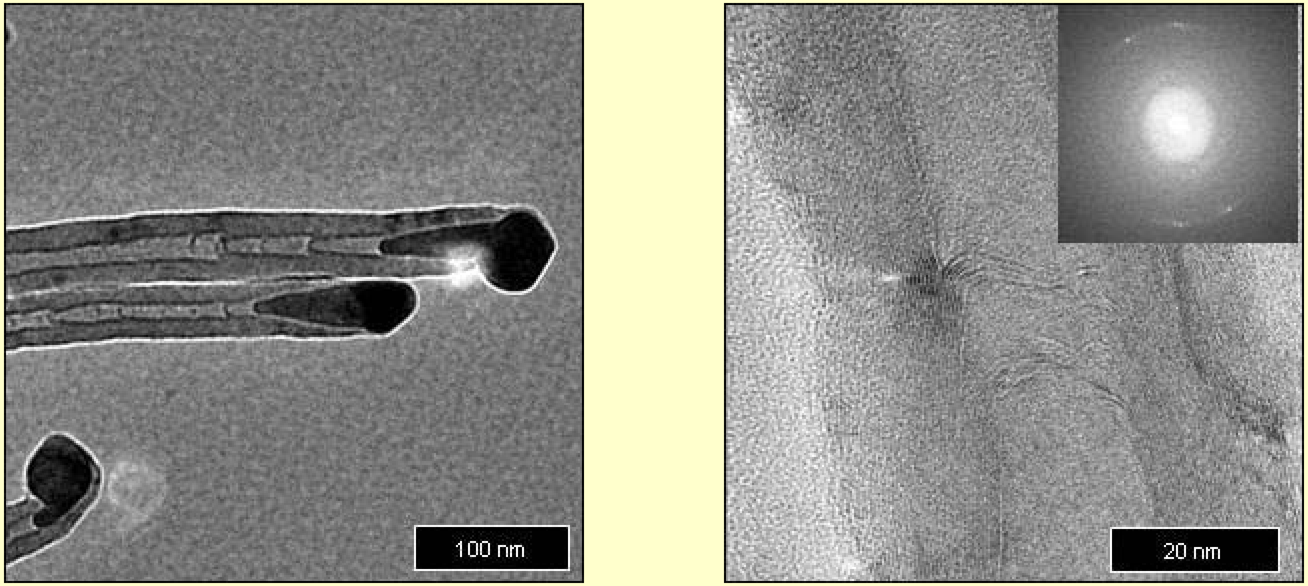
Activation with KOH or CO_2

Activated Nano-Structure Carbon.

Activated Nano-Structure Carbon.

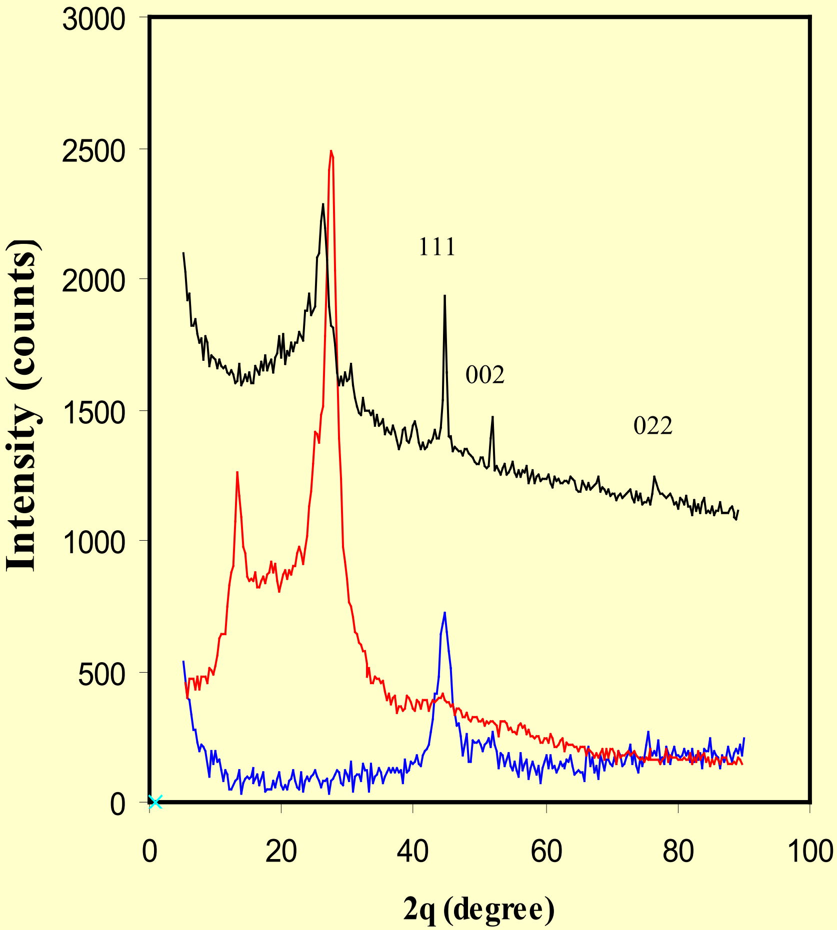


TEM images of carbon- Melem with with carbon- metal catalysts, synthesized at different carbonization time. The longer pyrolysis time (20 h) resulted in double the surface area than the shorter time one (2h). ~10 Ang. local pore.



(A) (B)

TEM image of nitrogen doped carbon--nanotubes. The metal catalyst particles are presented in the tips. Most of the catalyst particles are droplet-shaped with tails pointing inwards. (image A). The HRTEM image (B) reveals well organized carbon-tube wall formed by 30-35 sheets, some of which spilt out to form interlayers. The average lattice distance of 0.35 nm which is slightly larger than the one in graphite lattice (0.335 nm). It can be attributed to the substitution of larger size of nitrogen-catalyst atoms in the graphene network so the inter-space between graphene layers are slightly expanded.



X-ray deflection of Nit(—), Melem (—), and Nit- CNH-nanotube(—).

Table Theoretical composition of melem oligomers.

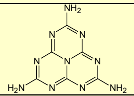
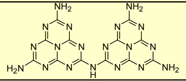
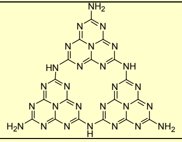
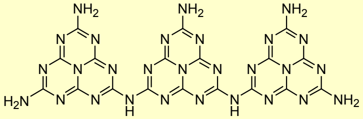
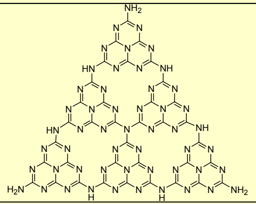
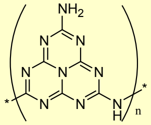
Structure	Chemical Formular	N/C	C wt%	N wt%	H wt%
	**$C_6N_{10}H_6$**	**1.666**	**33.03**	**64.22**	**2.83**
	**$C_{12}N_{19}H_9$**	**1.583**	**34.37**	**63.48**	**2.12**
	**$C_{18}N_{27}H_9$**	**1.50**	**35.82**	**62.69**	**1.52**
	**$C_{18}N_{28}H_{14}$**	**1.56**	**34.72**	**63.02**	**2.55**
	**$C_{36}N_{52}H_{12}$**	**1.444**	**36.86**	**62.34**	**1.03**
	**$C_{6n}N_{(9n+1)}H_{3((n+1)}$ (n ia the number of the melem units)**	**~1.54**	**-**	**-**	**-**
Carbon Nitride	**C_3N_4**	**1.334**	**39.13**	**60.87**	**0**

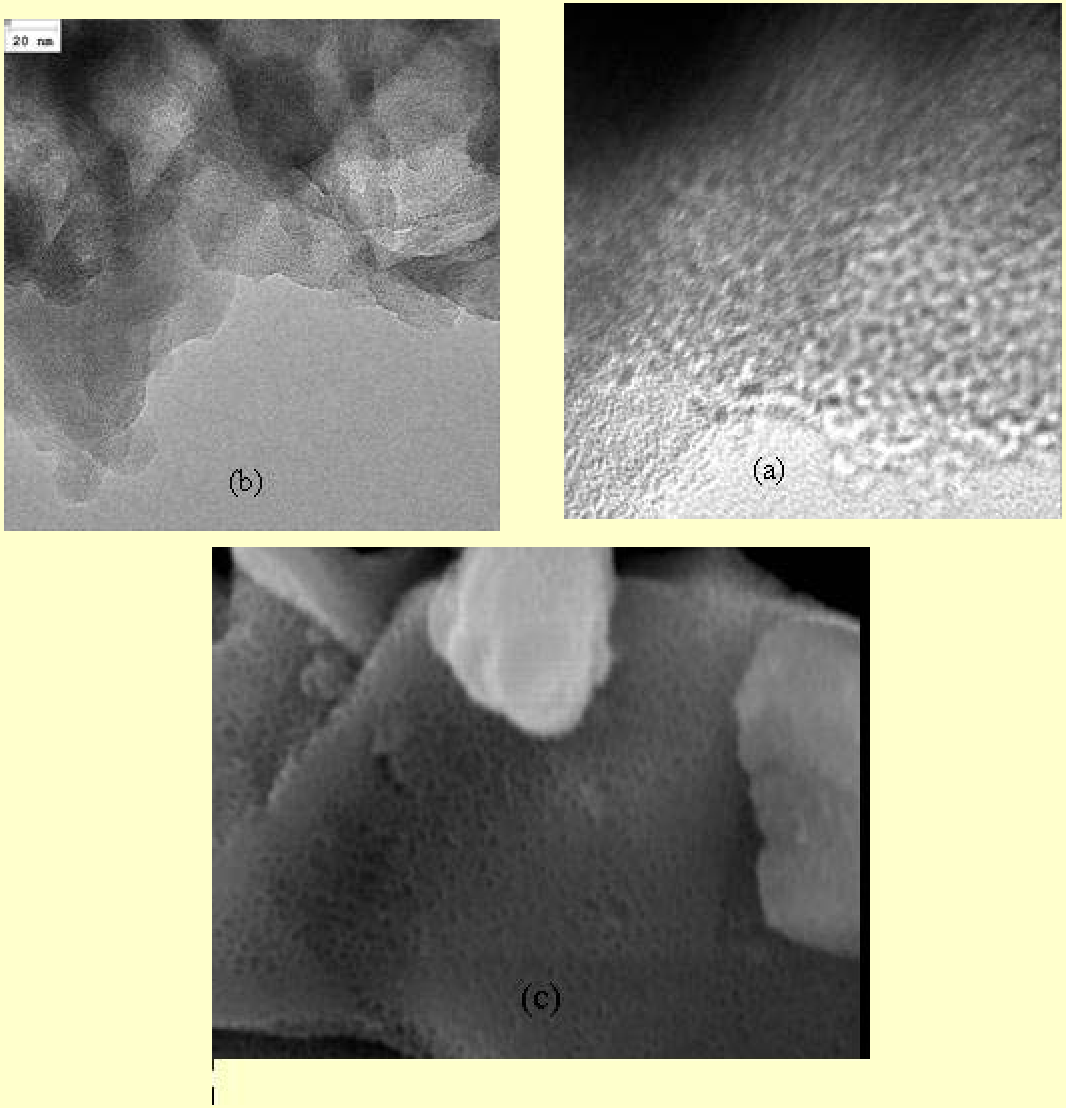
Table Elemental Analysis composition of melem oligomers.

Sample ID	H. wt%	C. wt%	N. wt%	N/C
Ma0145-2h	2.5	33.84	63.65	1.61
Ma0155-2h	1.36	35.87	62.76	1.49
Ma0165-2h	1.23	36.34	62.42	1.47
Ni60-6-20	1	63.2	7.3	9.94

Based on the elemental analysis results, and theoretical calculation (shown in last slide), Ma0145-2h, more likely have the linear structure. However, Ma0155-2h, and Ma0165-2h have N/C of ~1.50 which indicates that it's structure is close to triangle structure. As a confirmation, the C, N, H values are match the theoretical values (36.86%, 62.34%, 1.03%)

The surface area and hydrogen storage capacity of Melem based nit-carbon at 1 bar, 77K

Sample ID	S_{BET} (m^2/g)	H. C. (mL/g)
Ma015555-1	16.9	0.00
Ma015560-6	20.6	0.00
Ma015560-8	598.4	91.68
Ma015565-6	39.4	2.94
Ma015565-7	153.2	10.78
Ma015565-8	820.1	86.30
Ma015570-15	306.5	25.71
Ma015570-16	460.1	42.51
Ma015570-17	690.4	82.76
Nit65-1	94.6	14.30
Nit70-2	189.0	23.50



TEM image of polymer based carbon, The APK25-S1 has a pore size about 2 nm (a) the carbonization sample (b) gives minute pore size. SEM image (c) of Polymer carbon. It shown the small pore size pores evenly distributed in the carbon surface.

Porous Texture and Hydrogen Storage Capacity (77K, 1 bar) of Polymer-Based Activated Carbon

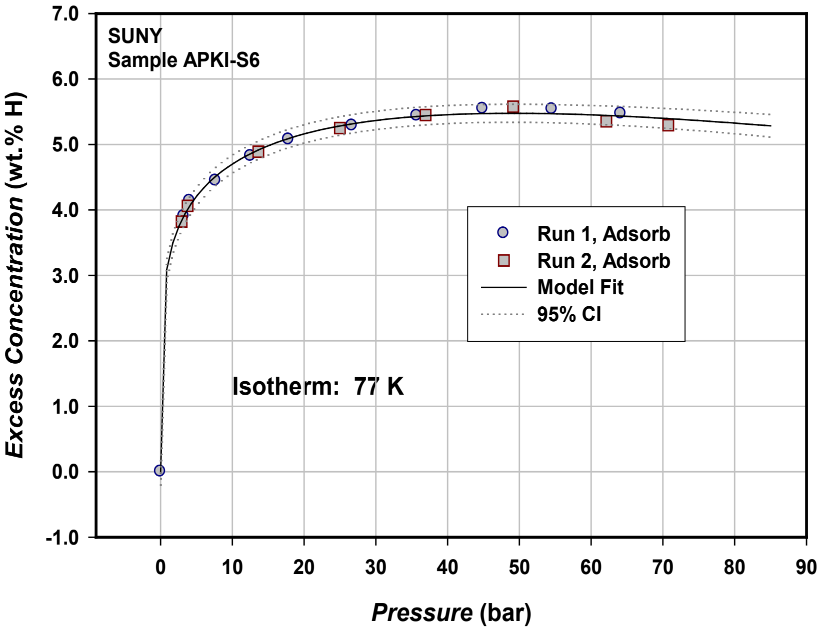
Sample	S_{BET} m^2/g	V_{pore} mL/g	V_{mp} mL/g	d_{DR} Å	ρ_a g/mL	$W(H_2)$ wt%	$V(H_2)$ gH_2/L
NitACP-119	1059	0.47	0.45	10.4	1.031	2.40	24.74
NitACP-121	2188	0.94	0.88	14.1	0.694	2.98	20.68
NitACP-109	2224	0.97	0.93	13.5	0.680	2.9	19.72
NitACP-127	2530	1.10	0.99	16.0	0.625	2.86	16.75
NitACP-133	2580	1.09	1.02	16.5	0.629	2.80	17.60
APKI-1	3255	1.71	1.24	20.0	0.444	2.93	13.02
APKI-4	3111	1.63	1.15	19.6	0.469	2.82	13.24
ACP-113	2315	0.97	0.93	15.3	0.680	2.97	20.16
ACP-125	3010	1.38	1.15	18.23	0.532	2.98	18.06
ACP-127	2530	1.10	0.99	16.0	0.625	2.86	17.88

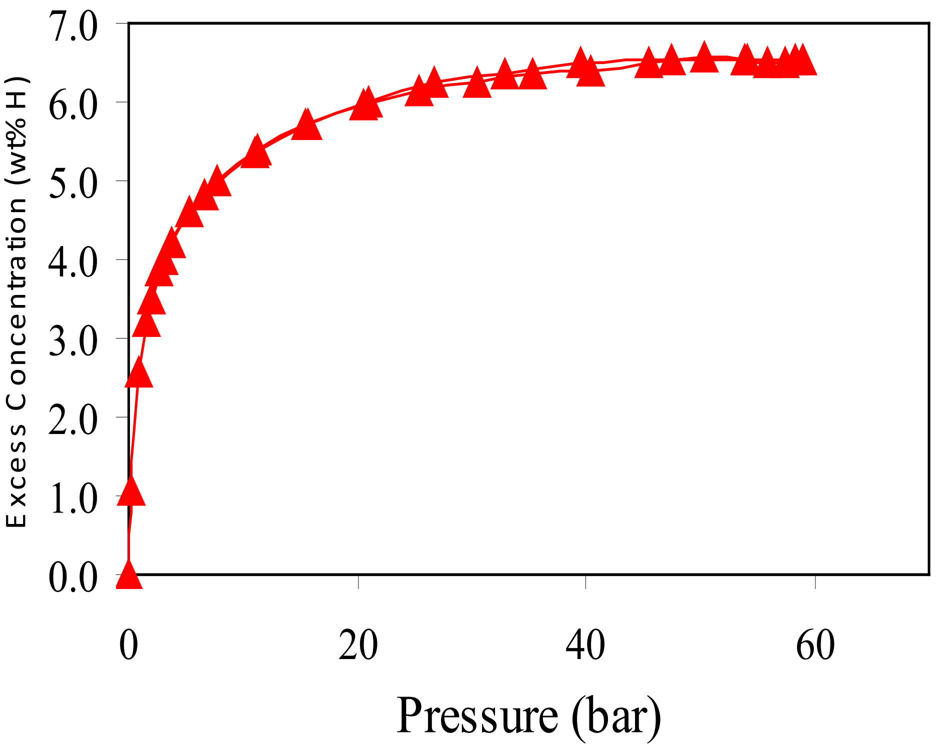
- The gravimetric hydrogen storage capacity achieved ~3.0 wt% at 77K 1bar.
- The volumetric hydrogen storage capacity achieved ~ 25gH_2/L at 77 K 1 bar.

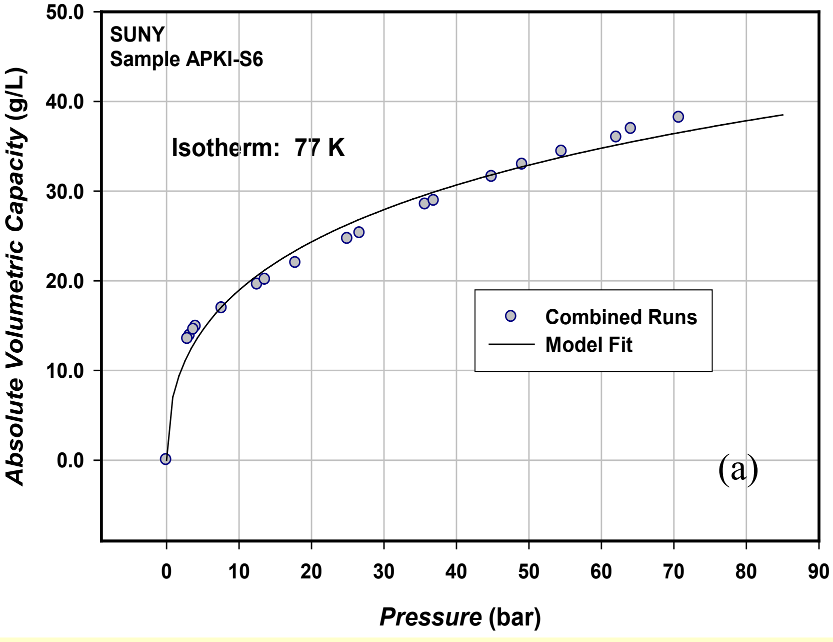
Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures

			H_2Uptake at 77K							
Sample	S_{BET} (m^2/g)	V_{tp} (cm^3/g)	0.1 MPa		1MPa		2MPa		4MPa	
			g/100g	g/L	g/100g	g/L	g/100g	g/L	g/100g	g/L
APKI-6	3034	1.22	2.98	19.6	5.38	30.7	6.02	34.4	6.52	37.3
APKI-2	3160	1.48	2.88	14.5	5.16	26.1	5.81	29.3	6.40	32.3
APKI-20	3070	1.17	2.80	16.8	5.40	32.3	5.74	34.4	6.01	36.0
APKI-3	3100	1.51	2.86	12.8	5.21	25.9	6.53	32.5	6.89	34.3
AP-R8	2550	0.99	2.35	16.2	4.81	32.3	5.37	36.0	5.58	37.5
AP-R20	3450	1.72	2.98	13.42	5.53	25.0	6.45	29.1	6.55	29.5

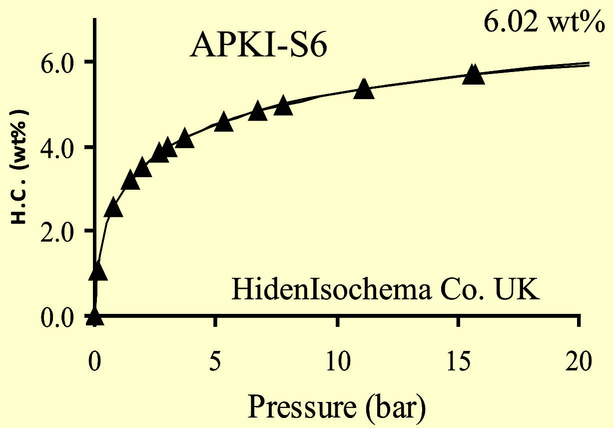
- The gravimetric hydrogen storage capacity achieved ~7.0 wt% at 77K 40 bar.
- The volumetric hydrogen storage capacity achieved ~ 38 g/L at 77 K 40 bar.

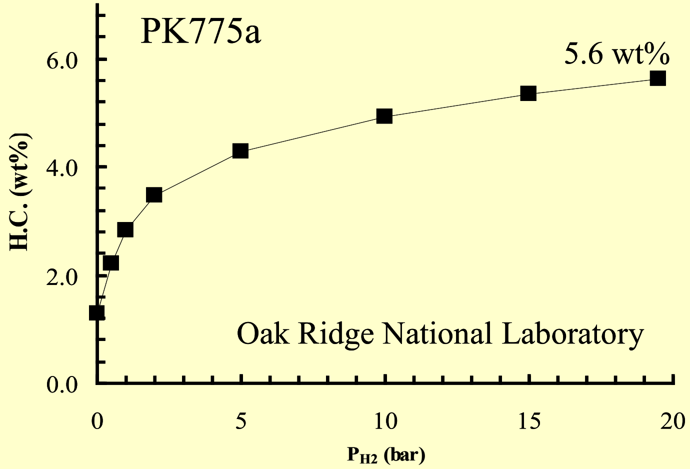


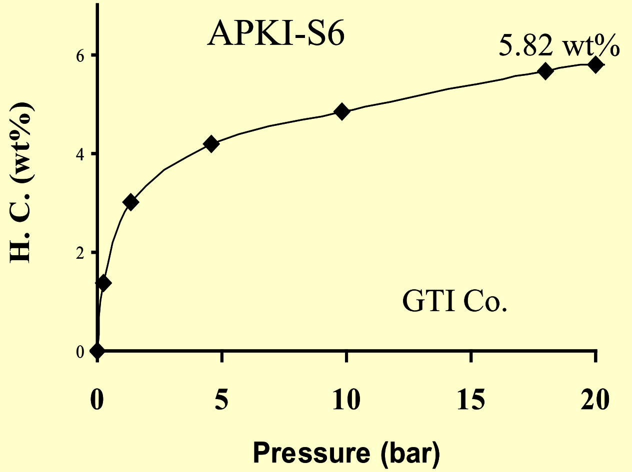


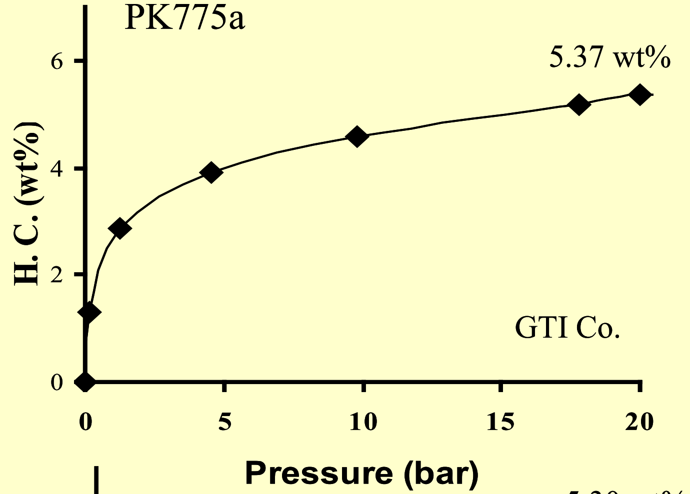


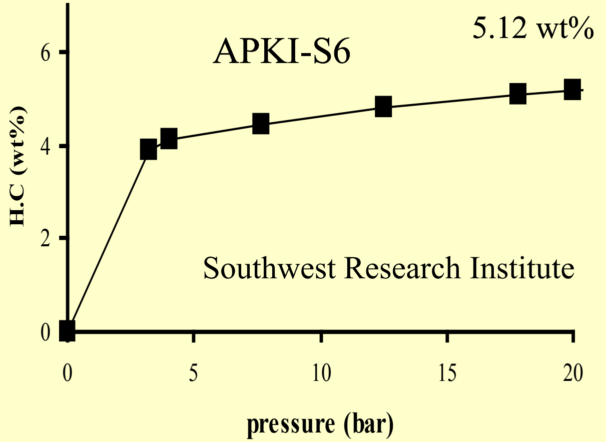
Results of measurements of APKI-S6; to the left from Southwest Research Institute (M.A. Miller), and above HidenIsochema Co. UK. Both shows a peak Gibbs excess concentration at 49 bar, 5.65 wt% for the former and 6.5 wt% later (b). (absolute volumetric capacity 39g/L at 70 bar Figure 1a.)



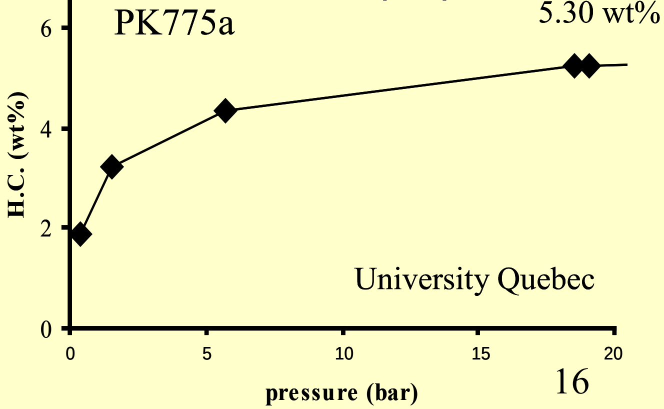


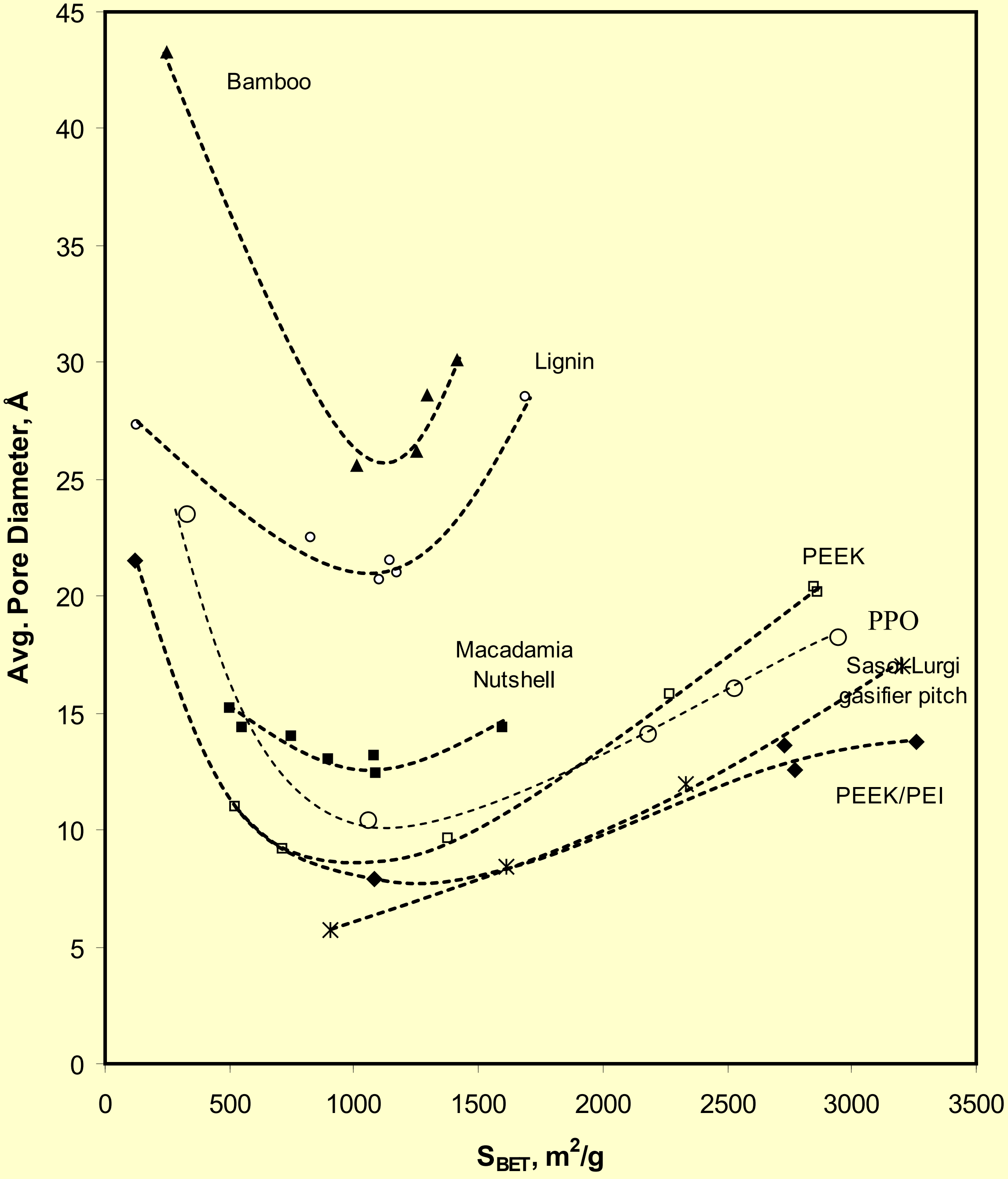






Comparison of Hydrogen uptake (at 77K, up to 20 bar) of APKI-S6 and PK775a The measured by Hidern Isochema Co. UK, GTI Co. and Southwest Research Institute





In all cases that we checked recently, The PEEK/PEI carbons blend have the narrowest pore size at the comparable surface area.

For example: for *Sbet* ~ 2500 - 3000 m2/g, the average pore diameter increases in the order of PEEK/PEI or PPO (~ 11- 14 Å), Sasol-Lurgi gasifier pitch (~12 - 17 Å), PEEK-carbon (~ 17 - 20 Å).

Similarly, for *Sbet* ~ 1000 - 1500 m2/g, average pore diameter increases in the order of PEEK/PEI (~ 8 Å), PEEK-carbon (~9 – 10 Å) or PPO, Macadamia Nutshell (~ 12- 14 Å), lignin (~ 20 - 30 Å), bamboo (~ 25 - 30 Å).

High surface area carbons could be achieved from all type of carbon precursors, the average pore diameter varies significantly.

Project Summary

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

<u>Approach:</u> **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 can be alloyed with active sites.

<u>Technical Accomplishments and Progress:</u>

- Detail study on composition and morphology of new type of carbon nanotube with Fe and and other metal into organo*cyclic-CNH*$_n$ *macromolecules rich with unsaturated bonds* that should be available RT application at moderate pressures for H_2 storage systems.
- Demonstrated synthesis of a modified polymer based carbons with high surface area and low average pore width. Accomplished gravimetric storage capacity of ~ 6.7-7.0 wt%, and volumetric capacity Achieve a high reproducibly on production in laboratory scale!
- New type of polymer based carbons with the corporation of metal ion a with high surface area and narrow pore size distribution were developed. The hydrogen storage capacity of ~3.0 at 77K, 1bar.

Future work

- **Continue to develop, modify, and characterize polymer materials**
- **Continue to develop Nanoporous carbons**
- **Continue to develop activated carbon with unsaturated functionalized polycyclic complexes.**
- **Improving the binding of hydrogen (adsorption) by corporation of metal clusters into Melem and polymer based activated carbons.**
- **Hydrogen adsorption tests at elevated temperature**