

Polymer-Based Activated Carbon Nanostructures for H₂ Storage

Israel Cabasso and Youxin Yuan

State University of New York

Polymer Research Institute at Syracuse N.Y.

May 20, 2009

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 structured carbons:

- High BET surface area $> 2600 \text{ m}^2/\text{g}$;
- High microporosity $> 95\%$;
- Average pore size $\sim 10 \text{ \AA}$;
- Hydrogen uptake: $\sim 7 \text{ wt}\%$ and $45 \text{ g H}_2/\text{L}$ at elevated Temperature;
- Increasing hydrogen storage temperature by introduction of active sites in the carbons with polycyclic triazine rings (polymelem).

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 H₂/L, with potential to meet DOE 2010 system-level targets.

Performance Measure	June, 2008 – May, 2009 performance Target
Carbon Surface Area and Pore Volume	$S_{BET} > 3000 \text{ m}^2/\text{g}$ $V_{mp} > 1.4 \text{ cc/g}$
Hydrogen Storage Capacity	Gravimetric Capacity (Material Based) >6 wt% 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

80% 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

70% 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)

60% complete

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).

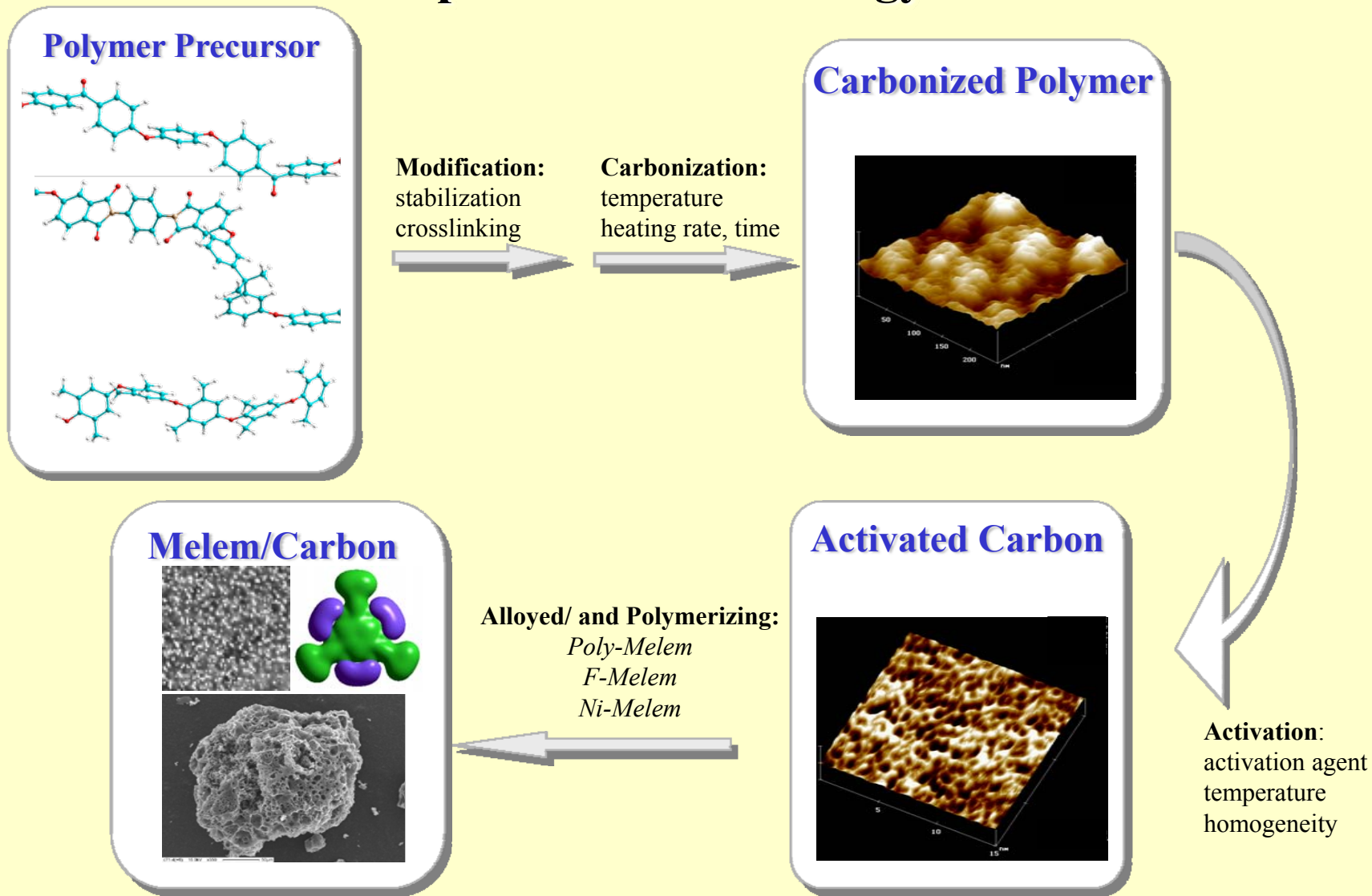
Task 4: Hydrogen Storage Testing

50% complete

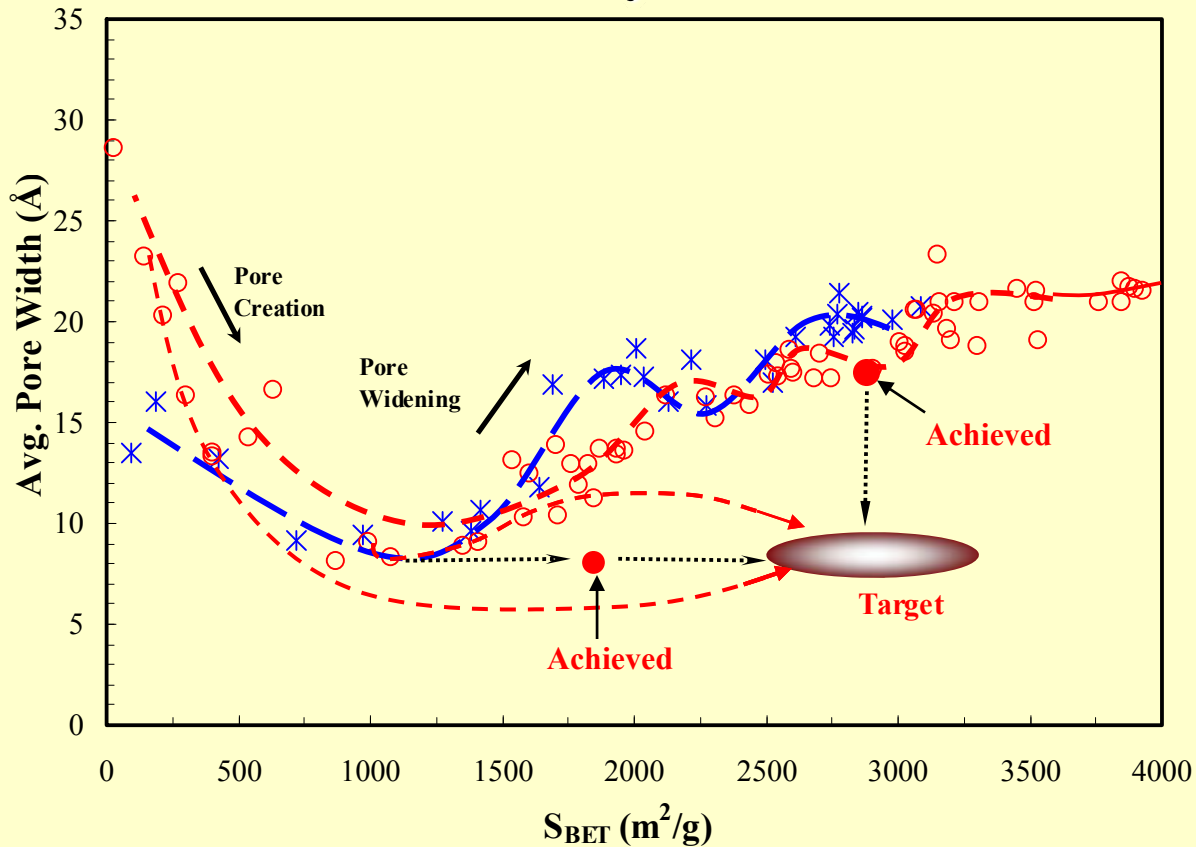
- Testing hydrogen adsorption the temp. range: 77K-300K and pressure of: 0.1 to 60 bar
- Testing durability of material in repeated runs.

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



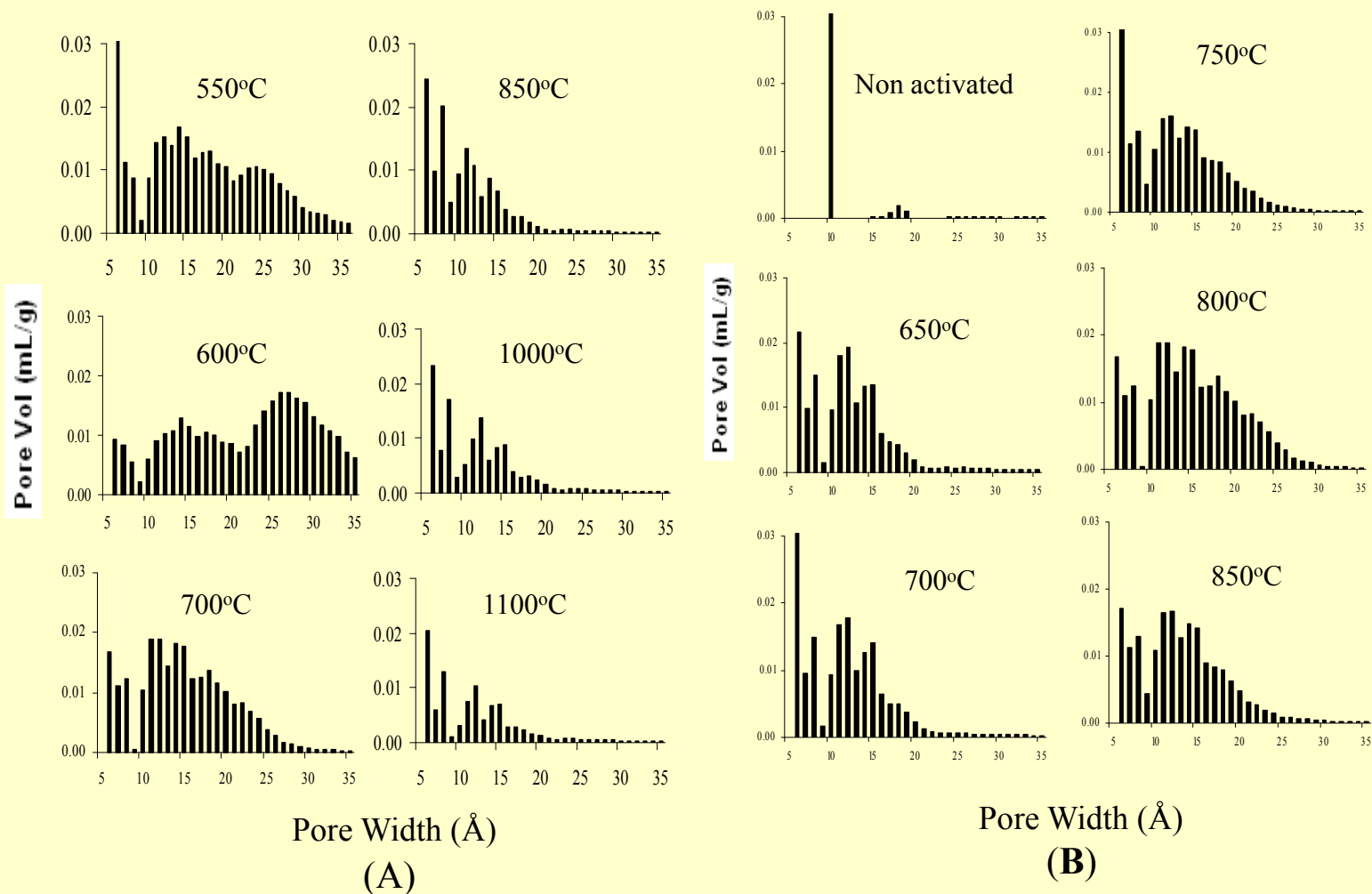
Correlation of Surface Area with Pore Size of Activated Polymer Carbons



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

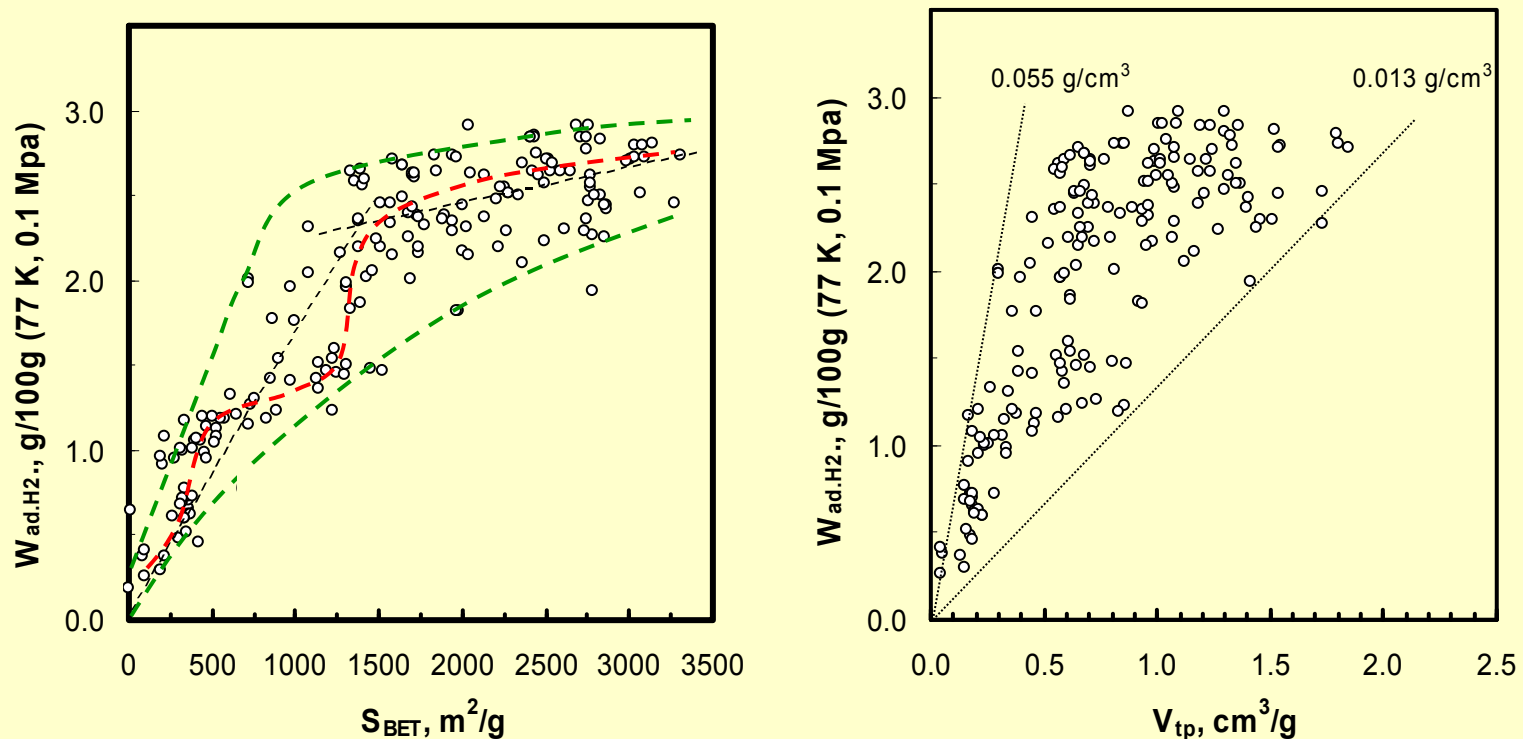
Achieved: $S_{BET} \sim 1850 \text{ m}^2/\text{g}$ with average pore width $\sim 8 \text{ \AA}$
 $S_{BET} \sim 3000 \text{ m}^2/\text{g}$ with average pore width $\sim 18 \text{ \AA}$

Pore Size Distribution as Function of Temperature

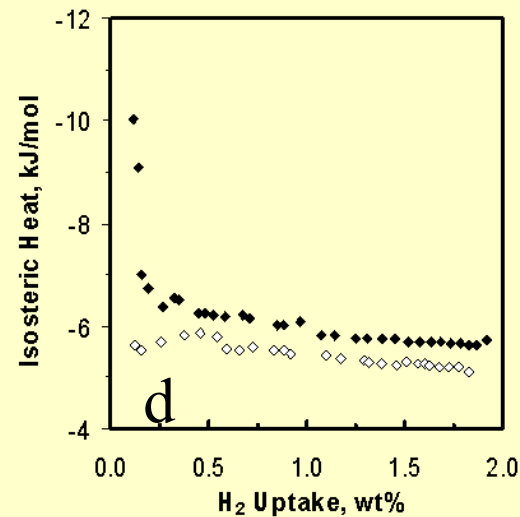
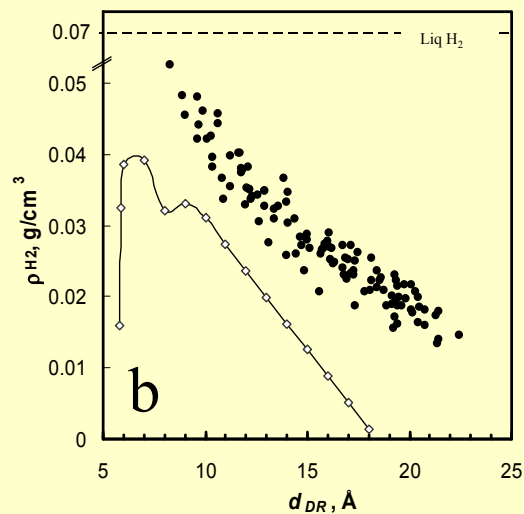
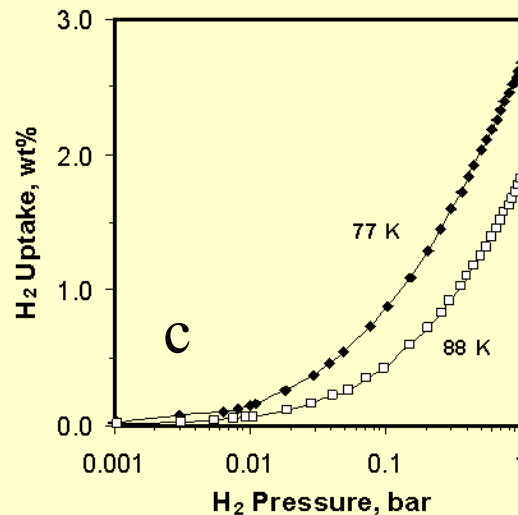
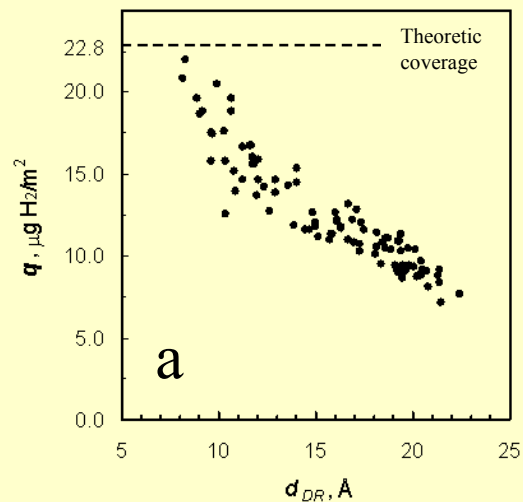


- (A). The structure and ordering can be controlled with augmentation of carbonization temperature. The structure ordering also narrows the pore size distribution.
- (B). Increase activation temperature (up to 800°C) leads to broadened pore size distribution, increases surface area and larger average pore diameter.

Correlation of Hydrogen Uptake with Carbon Morphology

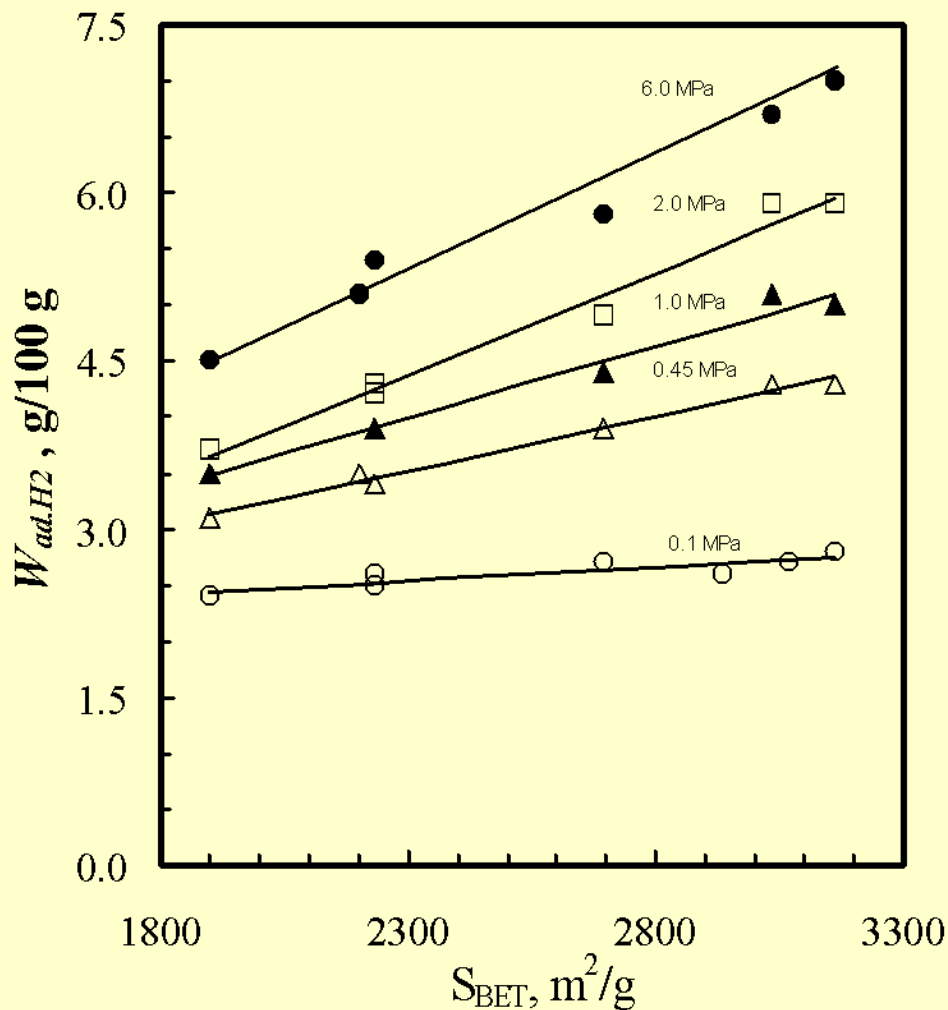


- For carbon with $S_{BET} \leq 1300$ m²/g, the gravimetric capacity increases linearly with S_{BET} at average surface coverage $\sim 16\mu\text{g H}_2$.
- For carbon with $S_{BET} \geq 1300$ m²/g shows a modest increase in hydrogen uptake up to $W_{H_2} \sim 3.0$ wt%
- The hydrogen density in pores varies from 0.013 g/cm³ to 0.055 g/cm³.



- **a.** Unit surface area hydrogen uptake at 77K and 1 bar achieved average surface coverage $21.9 \mu\text{g}/\text{m}^2$ at pore size $\sim 8 \text{\AA}$.
- **b.** The hydrogen density in pores at 77 K and 1 bar achieved $\sim 0.055 \text{ g/cm}^3$ (80% coverage).
- **d.** Isosteric heat of adsorption, $Q(\text{H}_2)$ is $\sim 5 - 6 \text{ kJ/mol}$, and 10 kJ/mol at lower pressure.

Correlation of Hydrogen Capacity with Surface Area at High Pressure and 77K



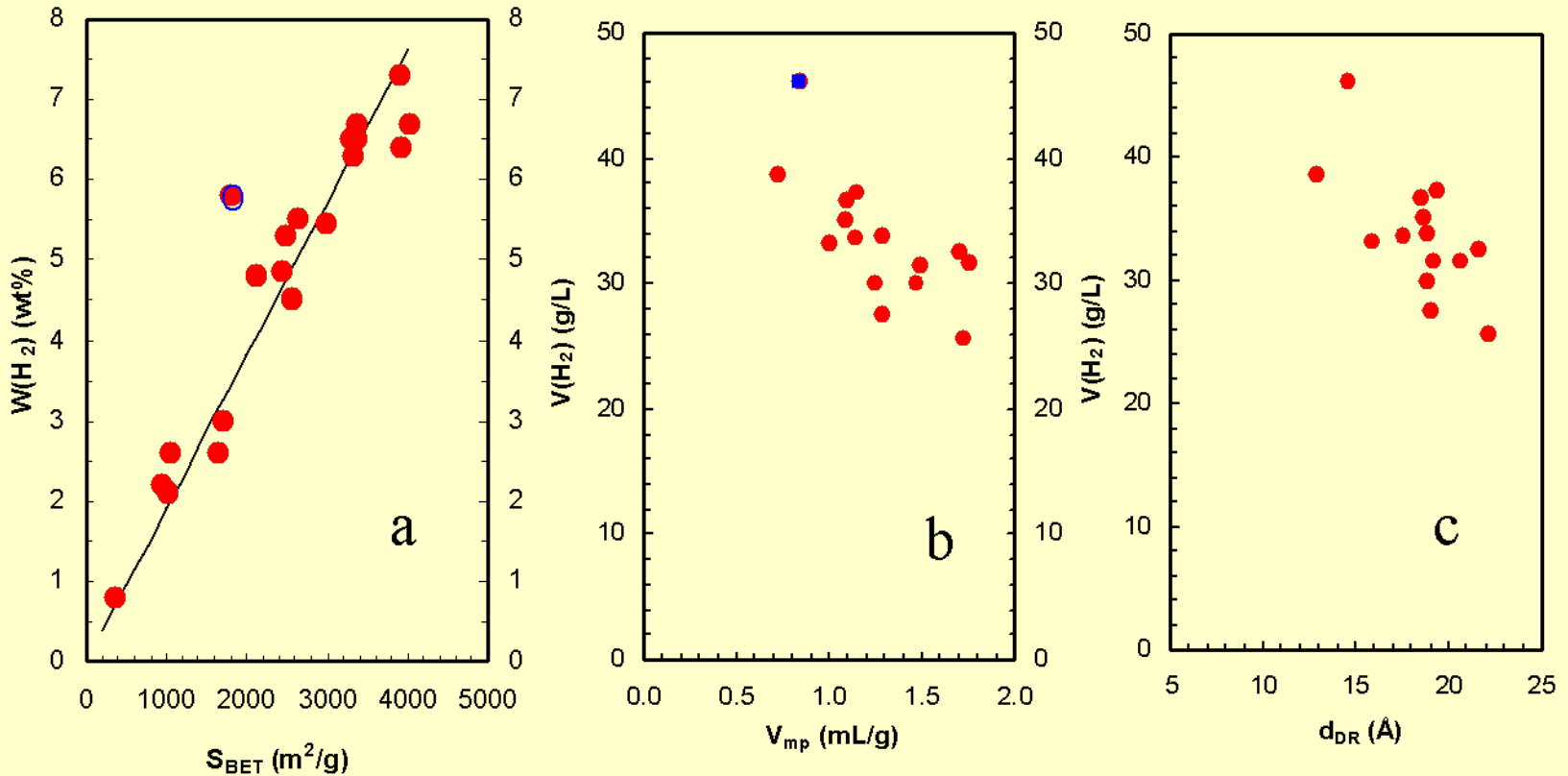
- Hydrogen uptake at 77K on polymeric carbon follows Langmuir adsorption.
- The correlation between hydrogen uptake and surface area S_{bet} (with at various H_2 pressure) increases linearly.

Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures

Sample	S_{BET} (m ² /g)	V_p (cm ³ /g)	H ₂ Uptake at 77K							
			0.1 MPa		1MPa		2MPa		6MPa	
			g/100g	g/L	g/100g	g/L	g/100g	g/L	g/100g	g/L
MPK-1	1800	0.84	2.0	14	3.5	26	4.5	34	5.8	43-46
MPK-2	1760	0.74	2.1	17	3.0	24	3.3	26	4.4	35
MPK-3	2000	0.90	2.4	17	3.5	25	3.7	26	4.5	32
MPK-4	2300	0.97	2.6	18	3.9	26	4.3	29	5.1	35
MPK-5	2720	1.15	2.7	16	4.4	26	4.9	29	5.8	35
MPK/PI-1	2110	1.03	2.8	18	4.5	29	4.8	31	5.0	33
MPK/PI-2	2430	1.03	2.8	18	4.4	29	4.8	31	4.7	31
MPK/PI-3	2775	1.28	2.7	15	4.7	26	5.3	30	5.4	30
MPK/PI-4	2890	1.29	2.6	14	4.7	26	5.3	30	6.4	36
MPK/PI-5	2935	1.36	2.6	13	4.5	24	5.1	27	5.9	31
MPK/PI-6	3035	1.81	2.5	11	5.1	22	5.9	26	7.4	32
MPK/PI-7	3095	1.60	2.7	12	4.8	22	5.5	26	6.4	30
MPK/PI-8	3160	1.98	2.8	11	5.0	20	5.9	24	7.0	28
MPPO-1	3920	2.20	2.7	10	4.8	18	5.3	20	6.4	24

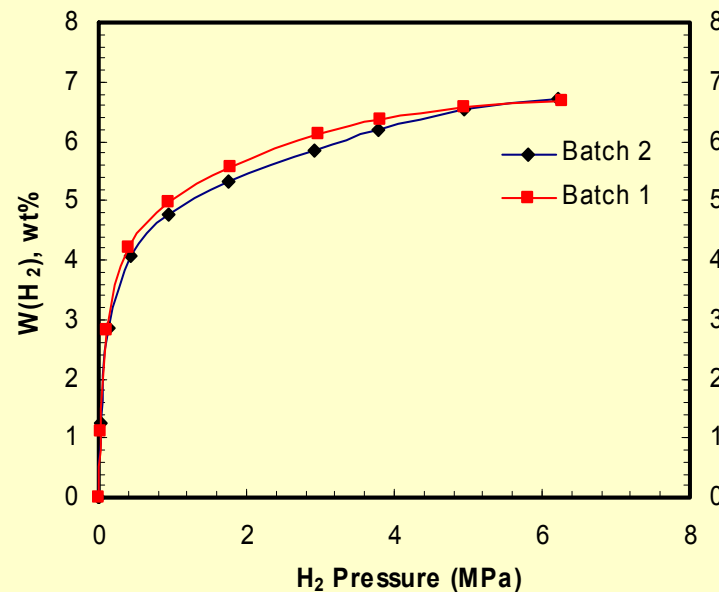
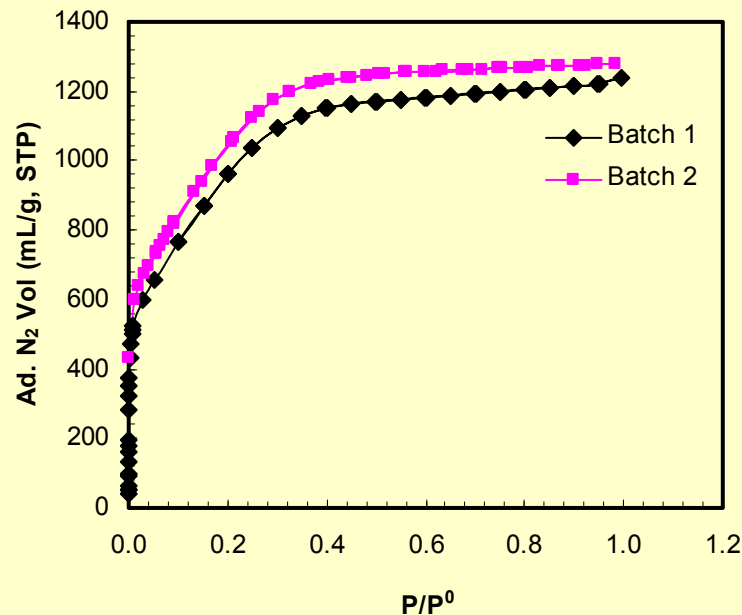
- The gravimetric hydrogen storage capacity achieved ~7.0 wt% at 77K 60 bar.
- The volumetric hydrogen storage capacity achieved ~ 40-45 g/L at 77 K 60 bar.

Hydrogen Storage Capacity of Polymer Derived Carbon Nanostructures



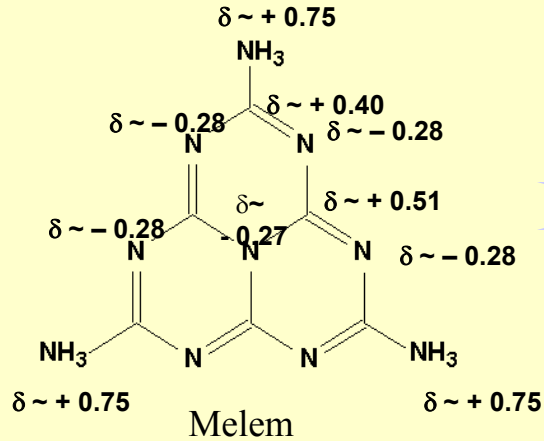
- **a.** Gravimetric hydrogen uptake increases linearly with surface area, at a rate of $\sim 20 \mu g H_2/(m^2/g)$, which indicates $\sim 6 H_2$ molecules occupy 20 graphene hexagon units.
- **b-c.** High volumetric hydrogen uptake (up to $46 g H_2/L$) is achieved at $V_{mp} \sim 0.8-0.9 mL/g$.

Reproducibility of Carbon Nanostructures Synthesized from Two Different Batches of MPK/PI Blend precursor

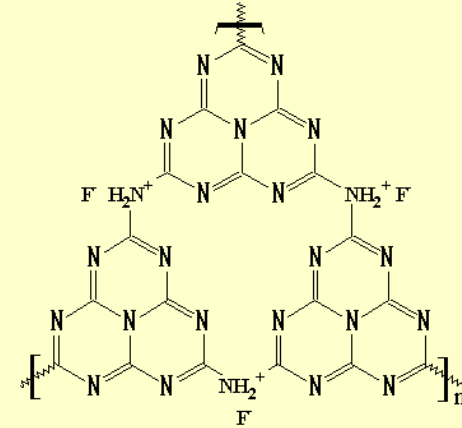


Batch of Material	S_{BET} (m ² /g)	V_{mp} (mL/g)	V_p (mL/g)	d_{DR} (Å)	$\frac{W(H_2), wt\%}{77 K}$
1	3070	1.23	1.82	20.1	6.7
2	3365	1.29	1.99	19.0	6.7

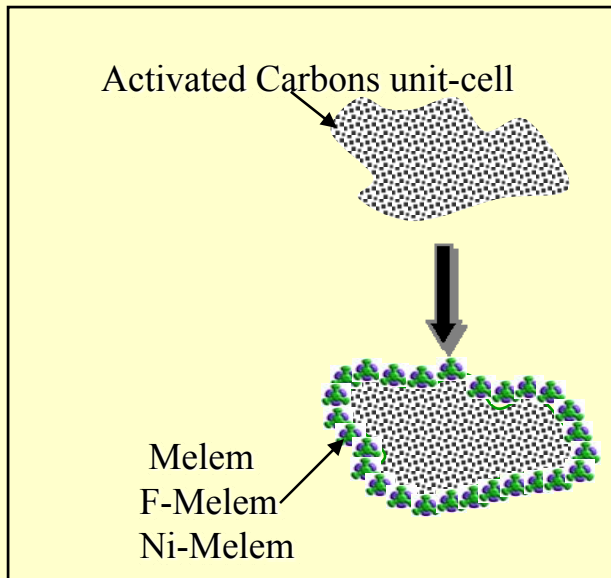
Poly - Melem Alloyed With Polymer Carbons



Fluorination

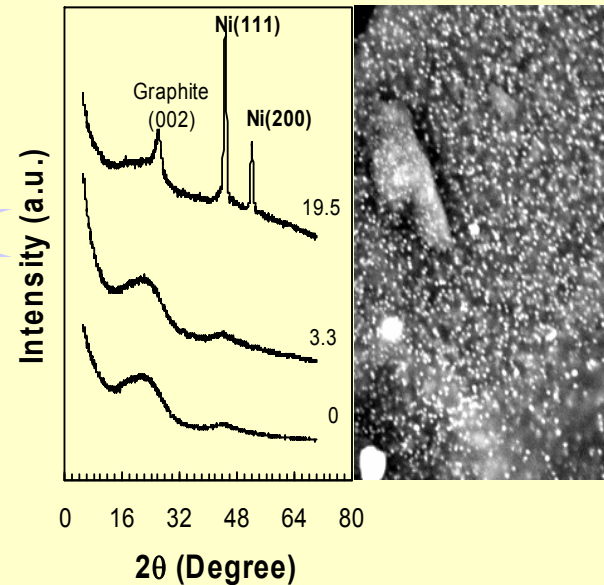


Ni- poly Melem-F
((tri-triazine rings))

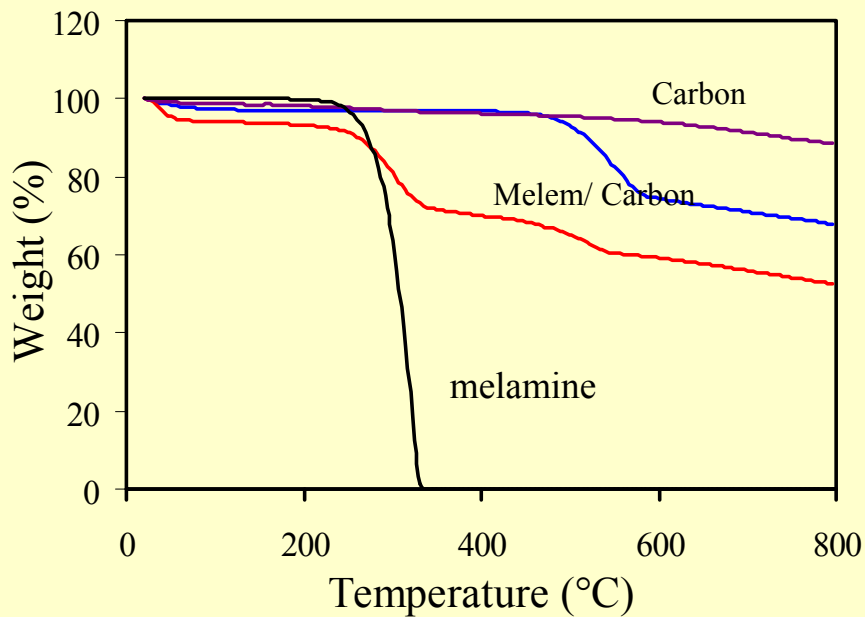


alloyed

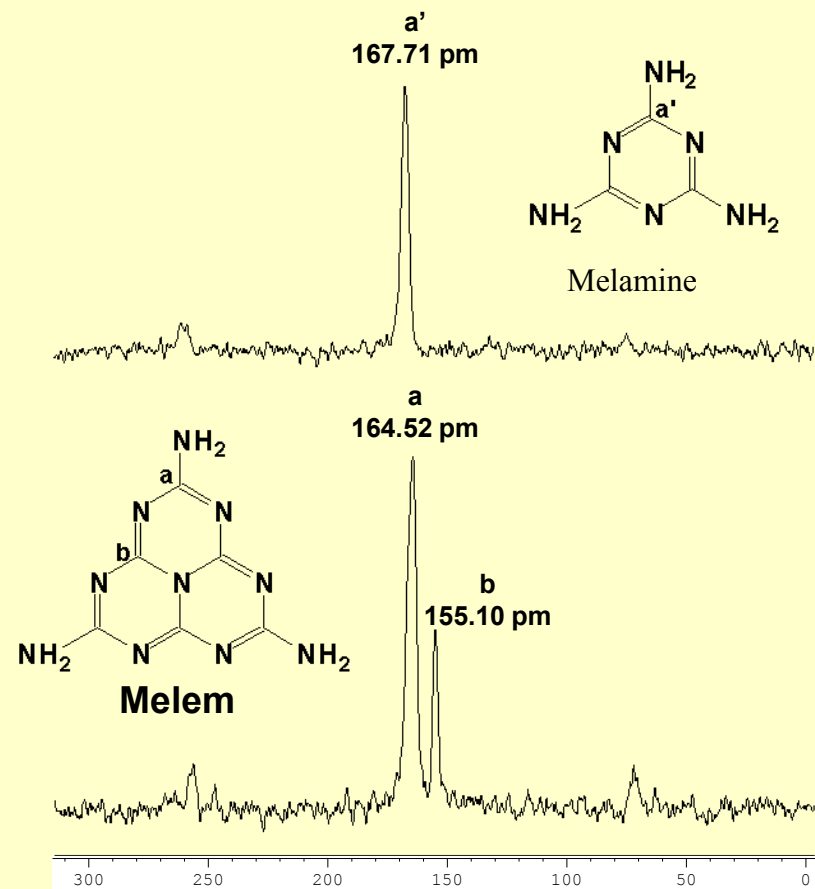
(Trace quantity
of co-catalyst Ni,
Fe)



Formation and Characterization of Melem/Carbon

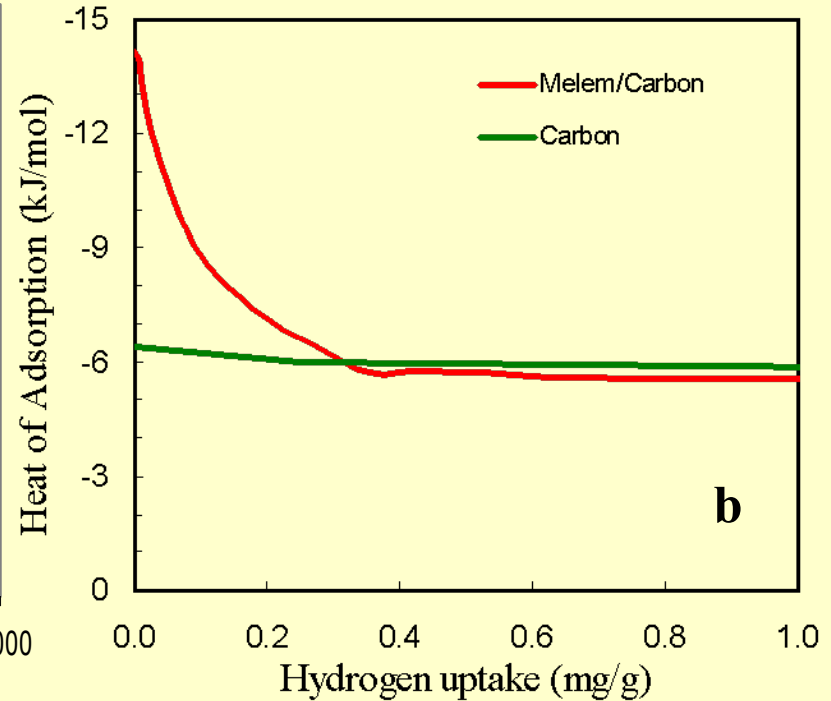
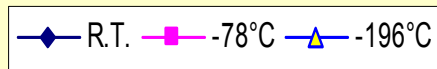
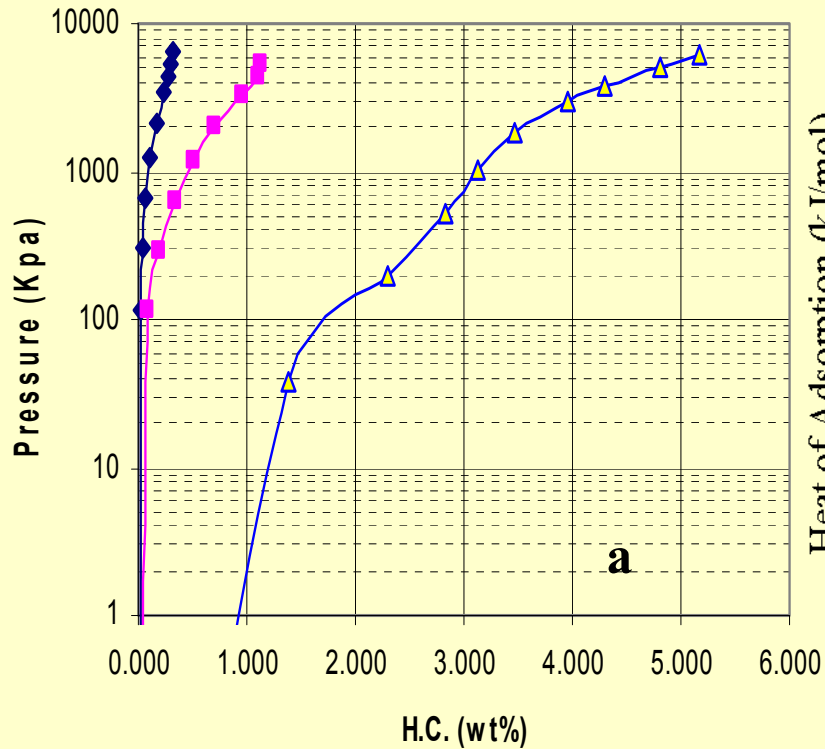


TGA Monitoring of Melem and $[\text{CNH}]_n$ formation within the Carbon



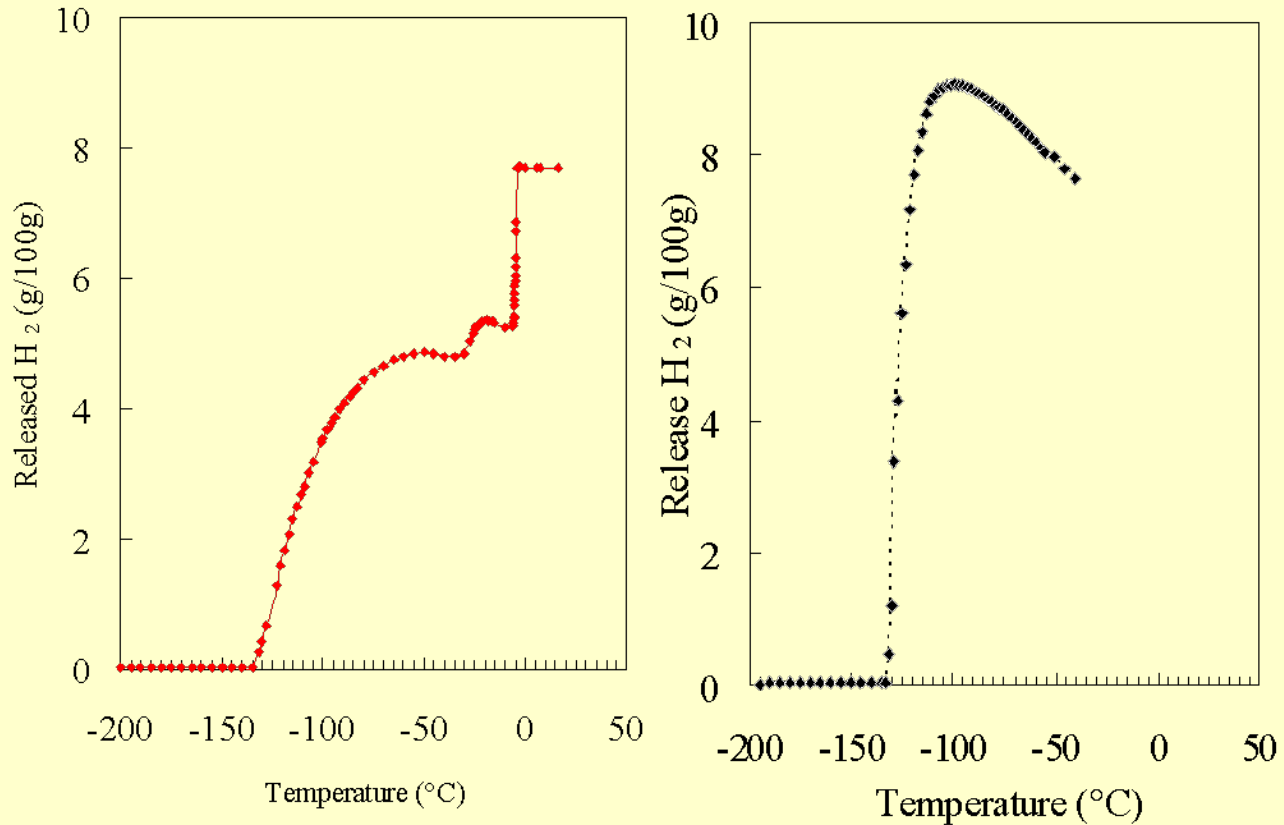
CP-MAS ^{13}C -NMR

Performance of Melem-Carbon Blend Alloy



- (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) Alloyed carbon with Melem or fluorinated Melem raises the hydrogen binding energy up to 14 kJ/mol at low pressure.

Hydrogen Storage By Solvated – Carbon Alloy



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

Carbon	<i>Porous Texture</i>				<i>Hydrogen Storage</i>		
	S_{BET} (m^2/g)	V_{mp} (mL/g)	V_{tp} (mL/g)	d_{DR} (\AA)	T_{de} ($^{\circ}C$)	W_{H_2} (wt%)	V_{H_2} ($g H_2/L$)
BP2000	1560	0.70	2.07	-	-	-	-
MPK-5	2720	1.10	1.15	17.2	-36	6.3	31.4
MPK/PI-9	2040	0.94	1.05	16.2	-50	4.7	23.4
MPK/PI-1	2120	0.98	1.06	16.3	-50	5.4	26.9
MPK/PI-10	2710	1.20	1.29	18.6	-36	5.6	27.9
MPK/PI-11	3300	1.46	1.85	19.0	-135	7.2	35.9
					-35	6.7	33.4
MPK/PI-12	3530	1.55	1.93	19.7	-36	8.0	39.9
					-65	5.6	27.9
MPK/PI-13	4020	1.75	2.29	21.7	-40	7.8	38.9
					-25	5.9	29.4

A gravimetric storage capacity of up to 8.0 wt%, and a volumetric storage capacity of up to ~ 40 g H₂/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-CNH_n 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.**