

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 $> 2600 \text{ m}^2/\text{g}$;
- High microporosity $> 95\%$;
- Average pore size $\sim 10 \text{ \AA}$;
- Hydrogen uptake: $\sim 7 \text{ wt\%}$ and $45 \text{ g H}_2/\text{L}$;
- Increasing hydrogen storage temperature by doping carbons with multicyclic ligands.

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

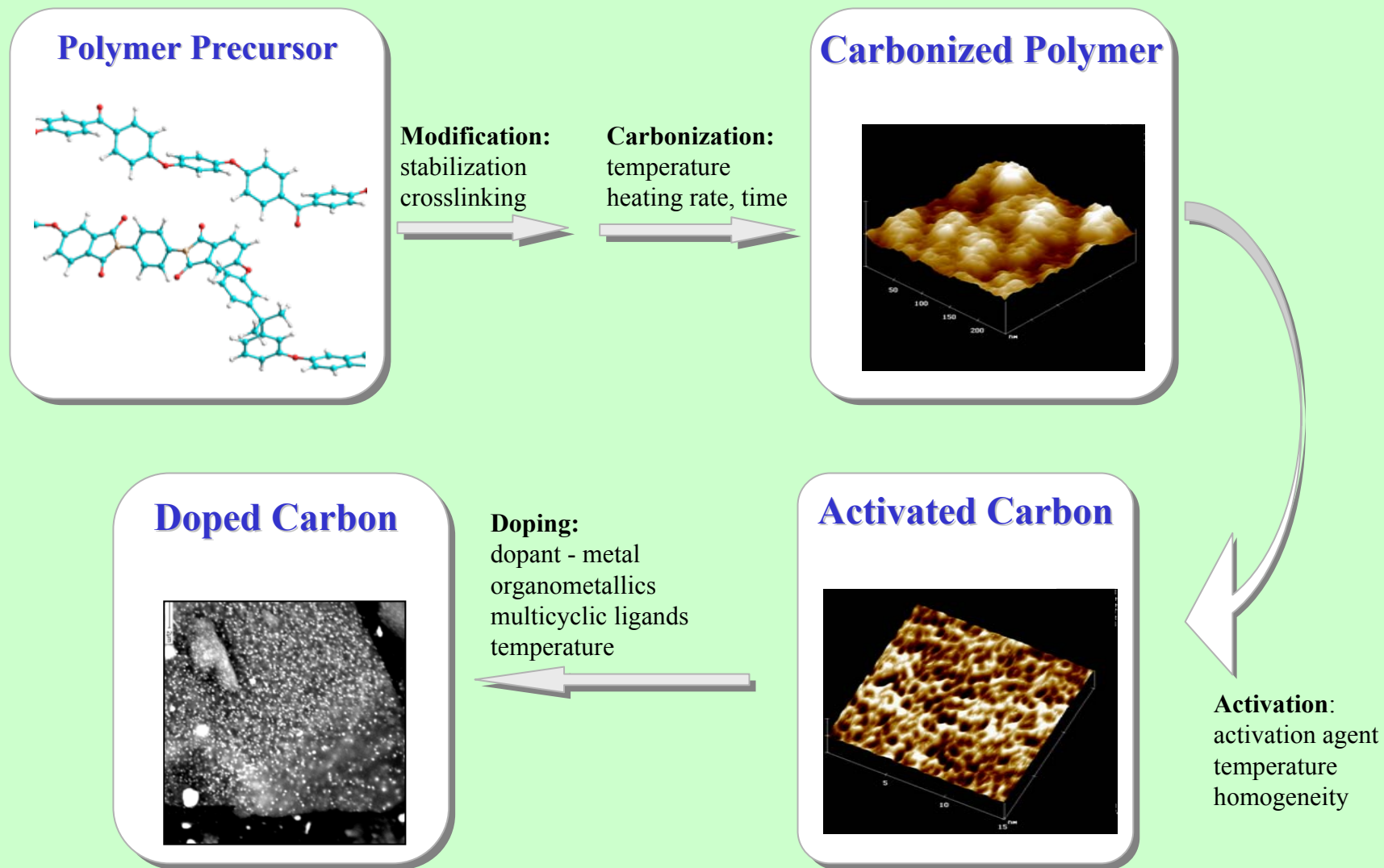
Processing the precursors (MPPO, MPEEK and PEI) at high melt shear rates further controls the morphology and orientation of crystalline regions.

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.

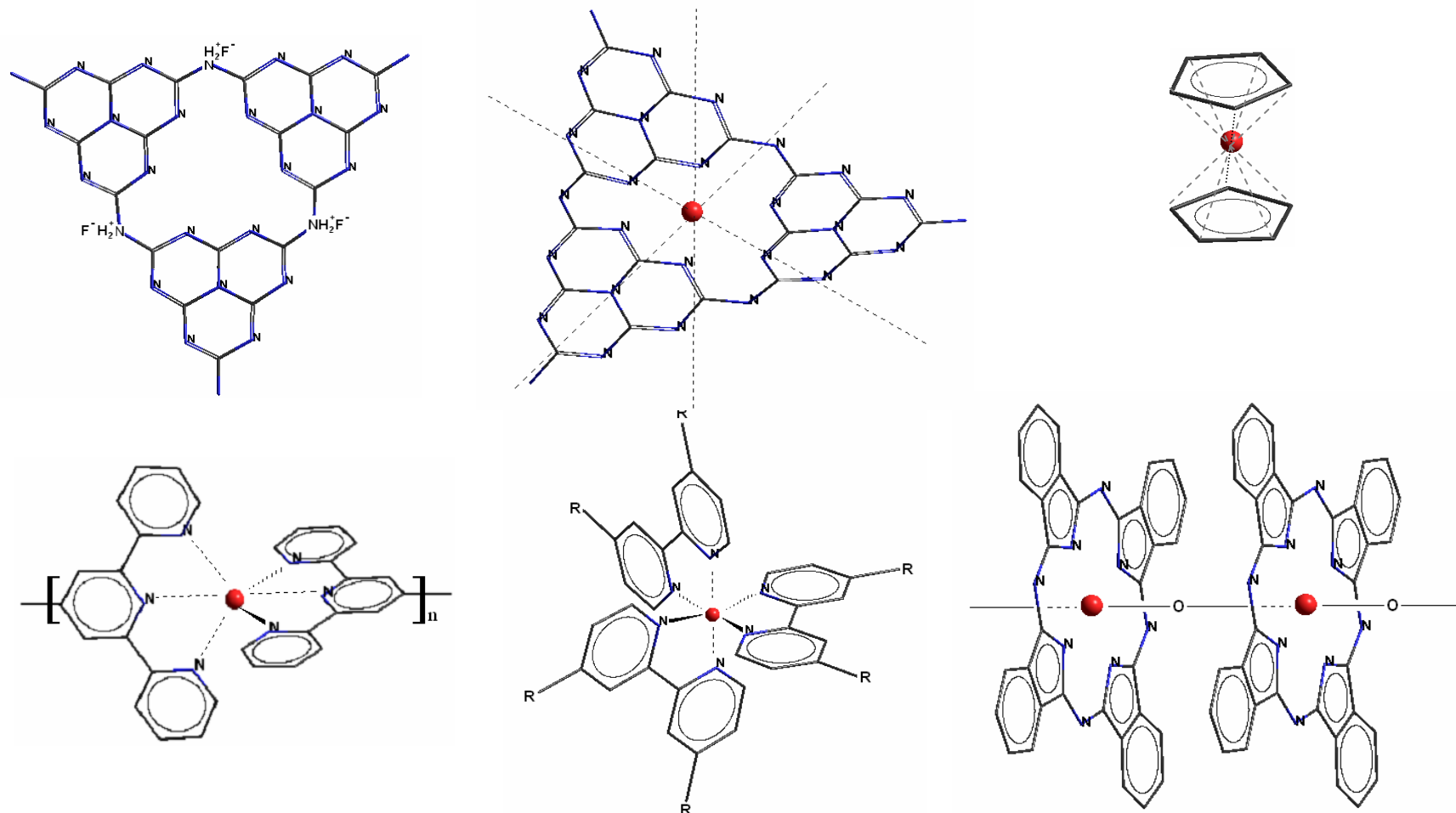
Physisorption in carbon/polymer Conduct H₂, N₂ and He adsorption measurements. Study and correlate *surface area, ultramicropore volume, pore size distribution* and *storage* to the **methods of the carbon synthesis**.


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



Organometallic and Multicyclic Ligand Dopants



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

Correlation of Surface Area with Pore Size of Activated Polymer Carbons

Formation of porous structure

1st Stage Burn-Off: pore creation dominates → higher surface area, smaller pores;

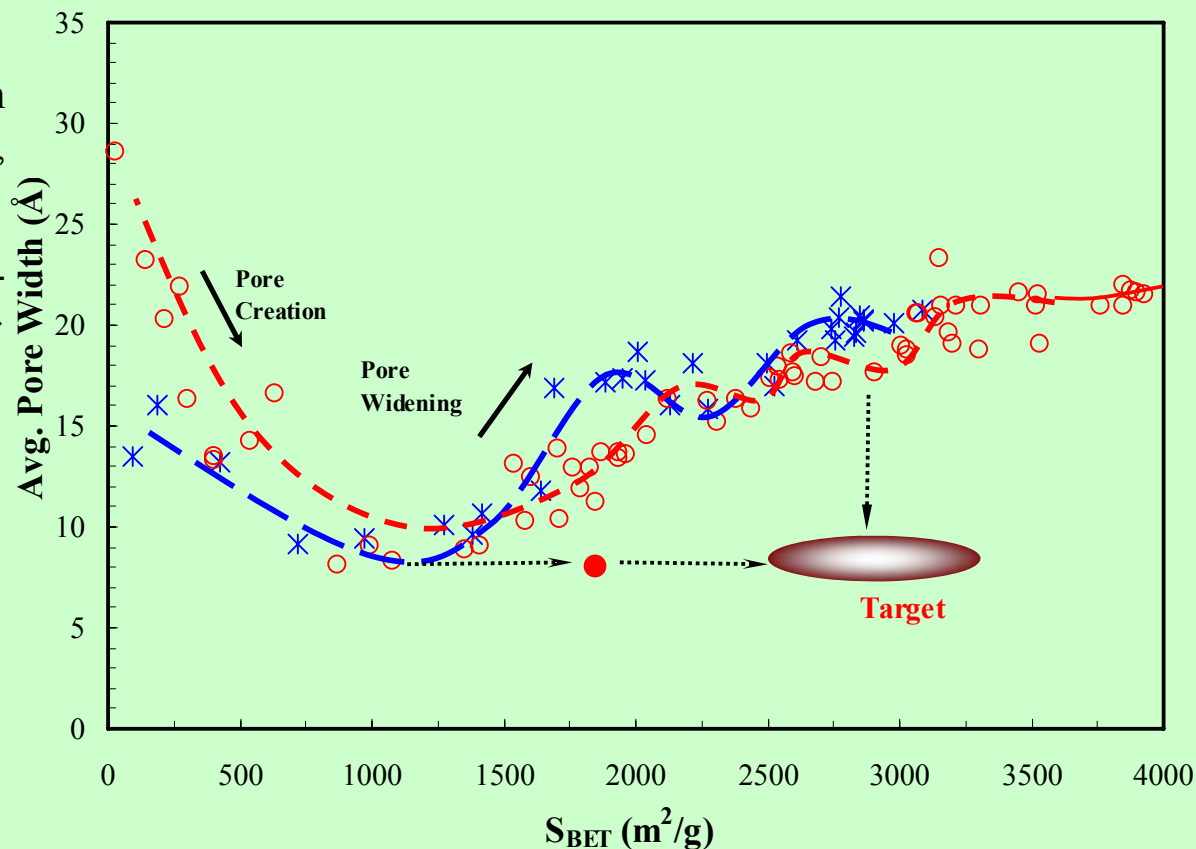
2nd Stage Burn-Off: pore enlargement and fusion dominate → higher surface area, larger pores.

Target:

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

Achieved (●):

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



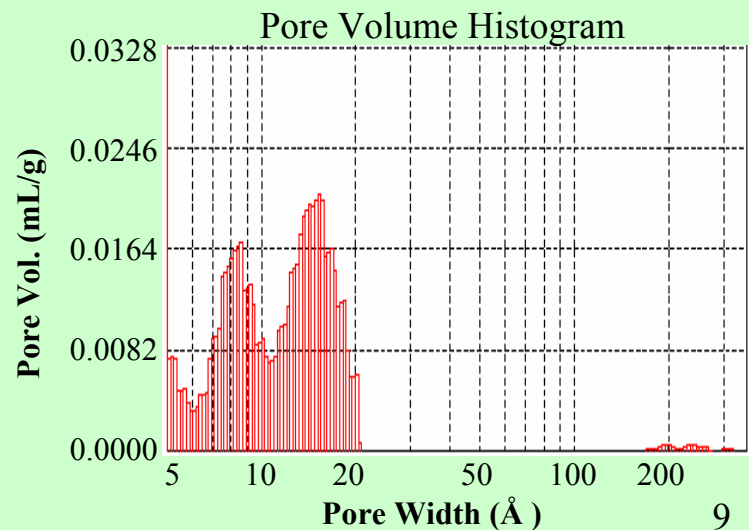
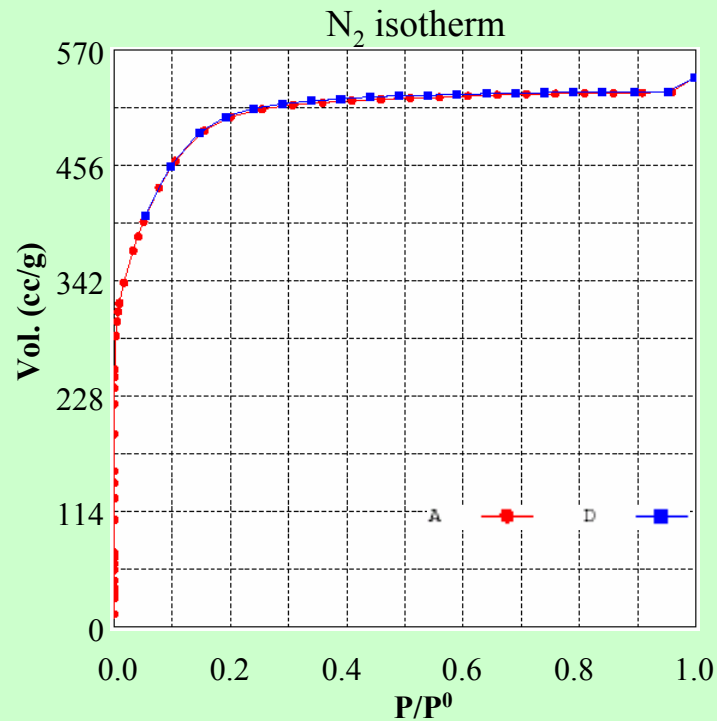
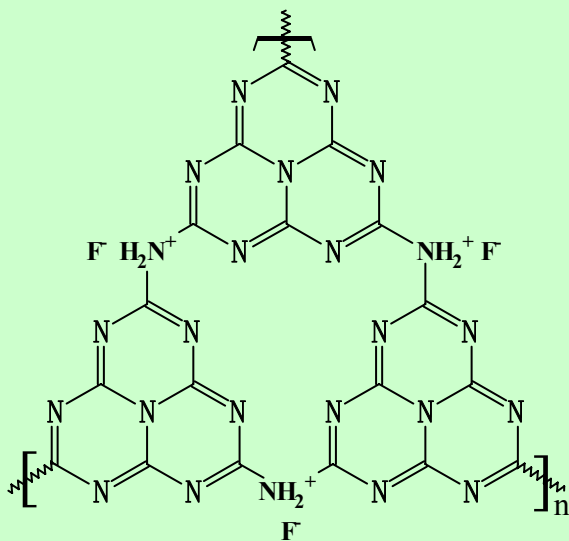
All points represent experimental data

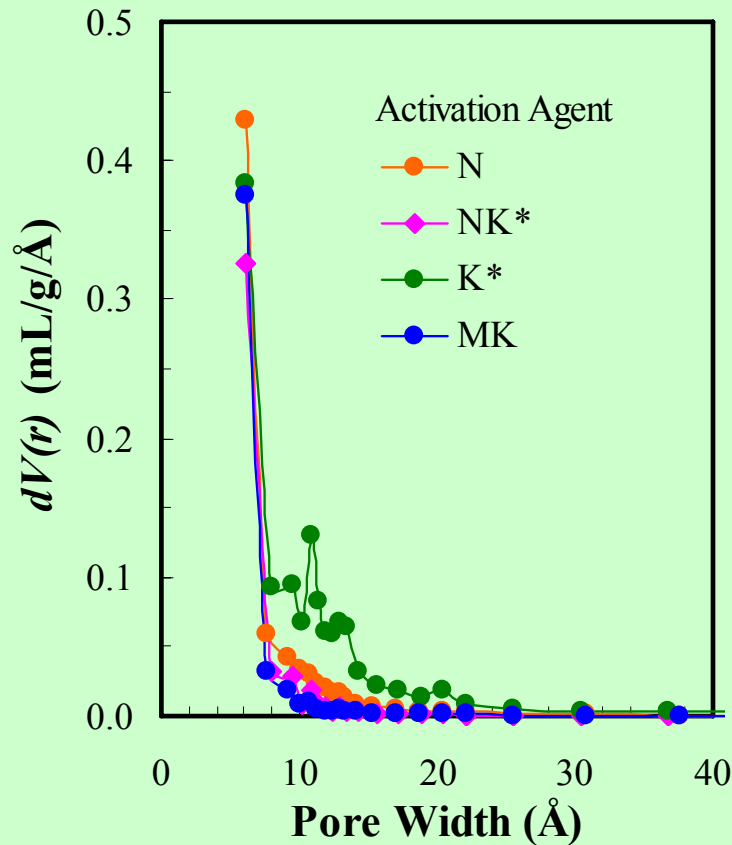
[CNH]_n doped high surface area polymer carbon

BET surface area: 1850 m²/g

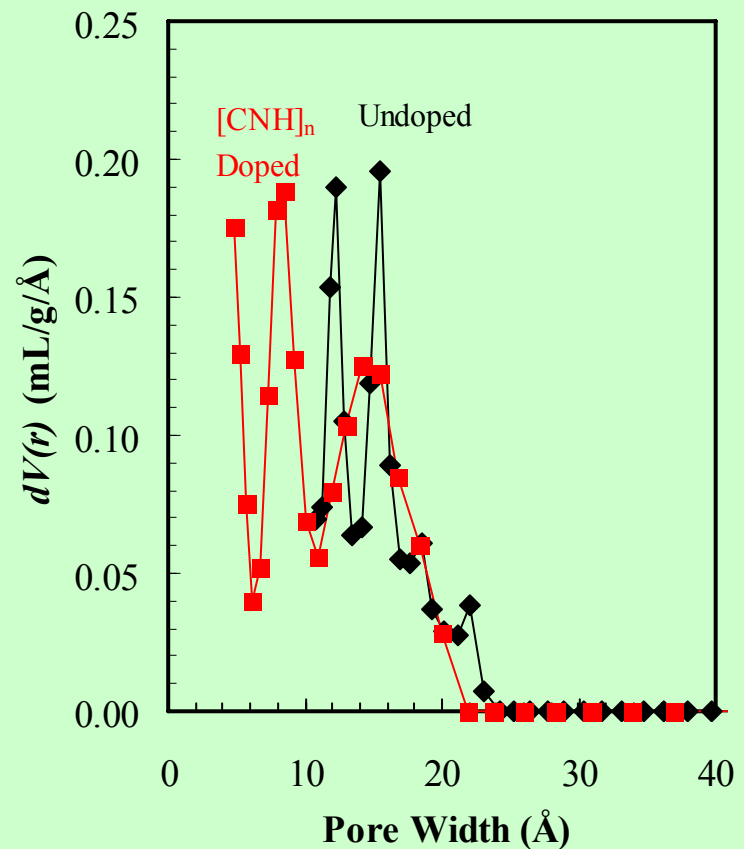
Pore Vol.: 0.84 mL/g

Average Pore Width: 8.52 Å

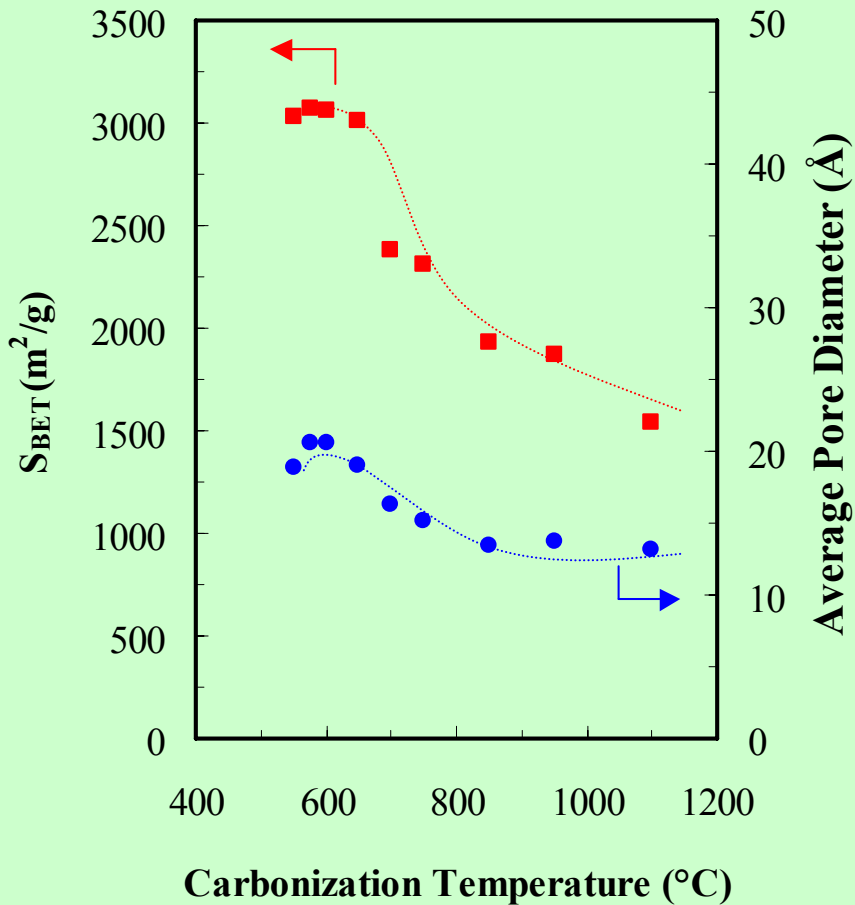




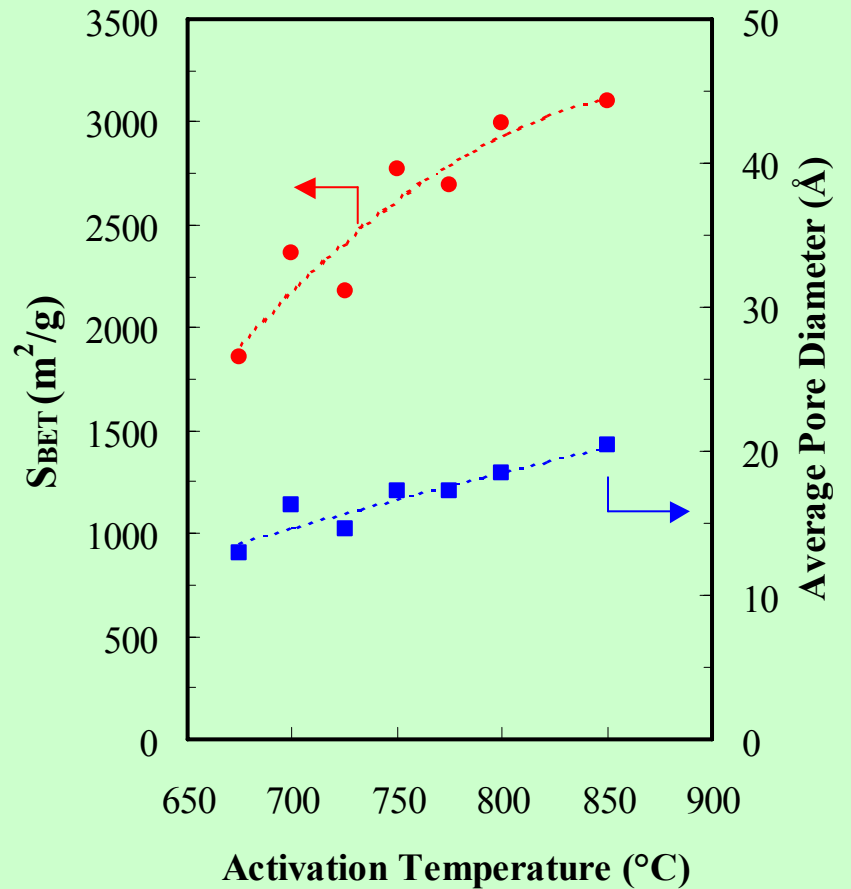
Strategy I: Develop a set of activation agents. Activation agent MK has a better affinity to carbon matrix, allowing homogeneous activation and, hence, narrow pore size distribution.



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.

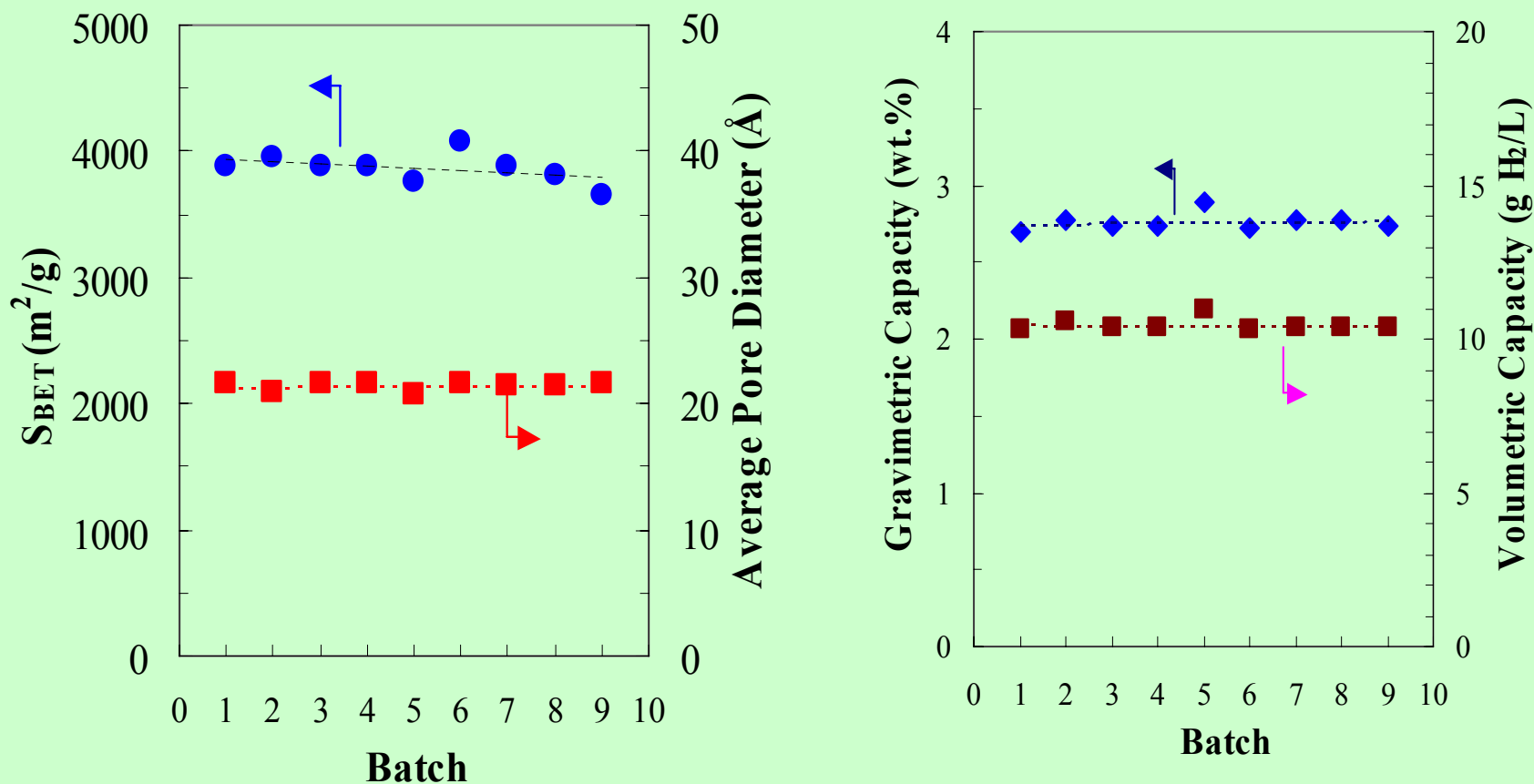


Strategy III: Adjusting carbonization temperature. Carbonization at 600-800 $^{\circ}C$ achieves the desired pore diameter and surface area.

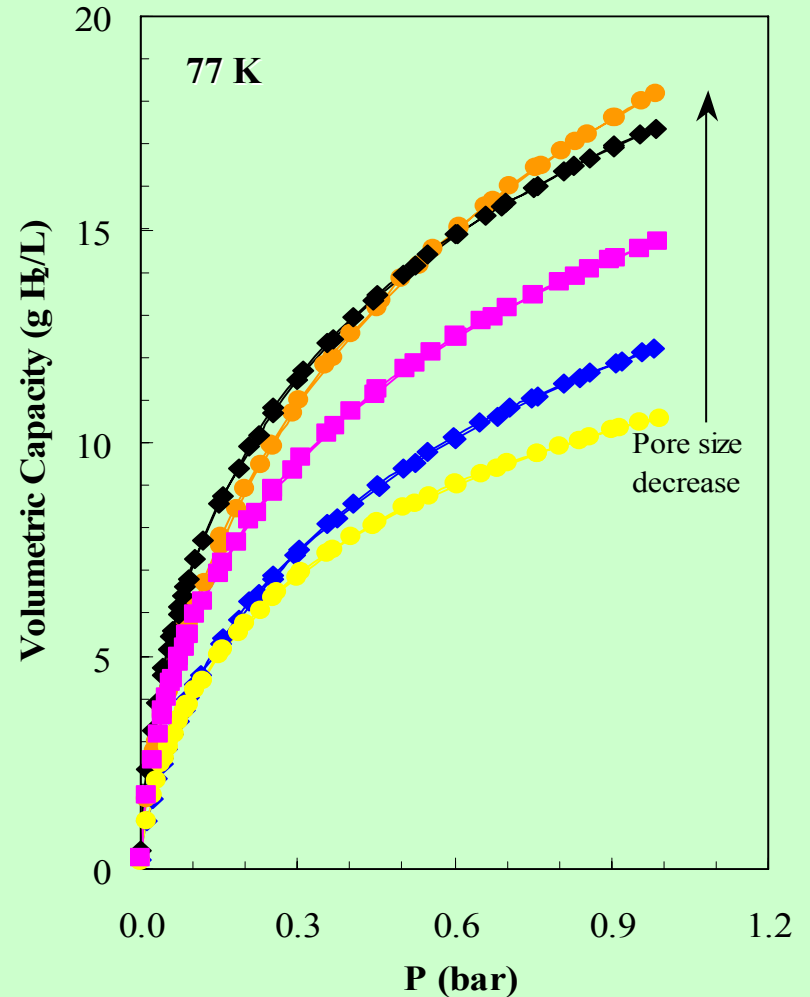
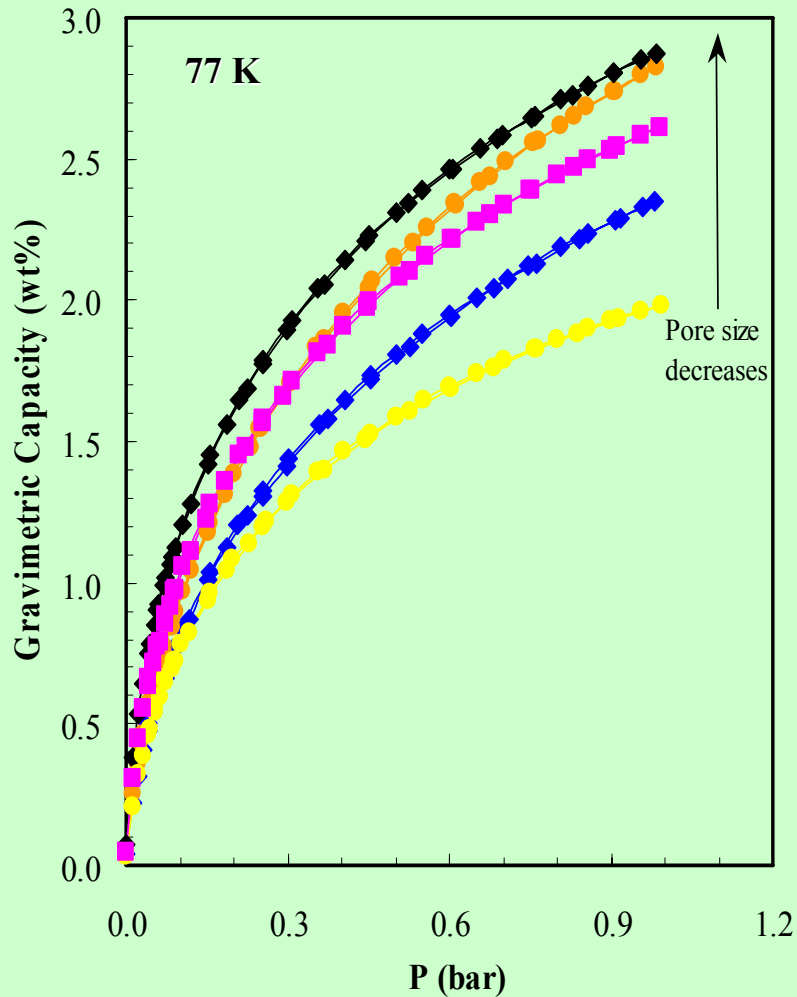


Strategy IV: Adjusting activation temperature to achieve the desired pore diameter and surface area.

Reproducibility of the Production of Activated Polymer Carbons

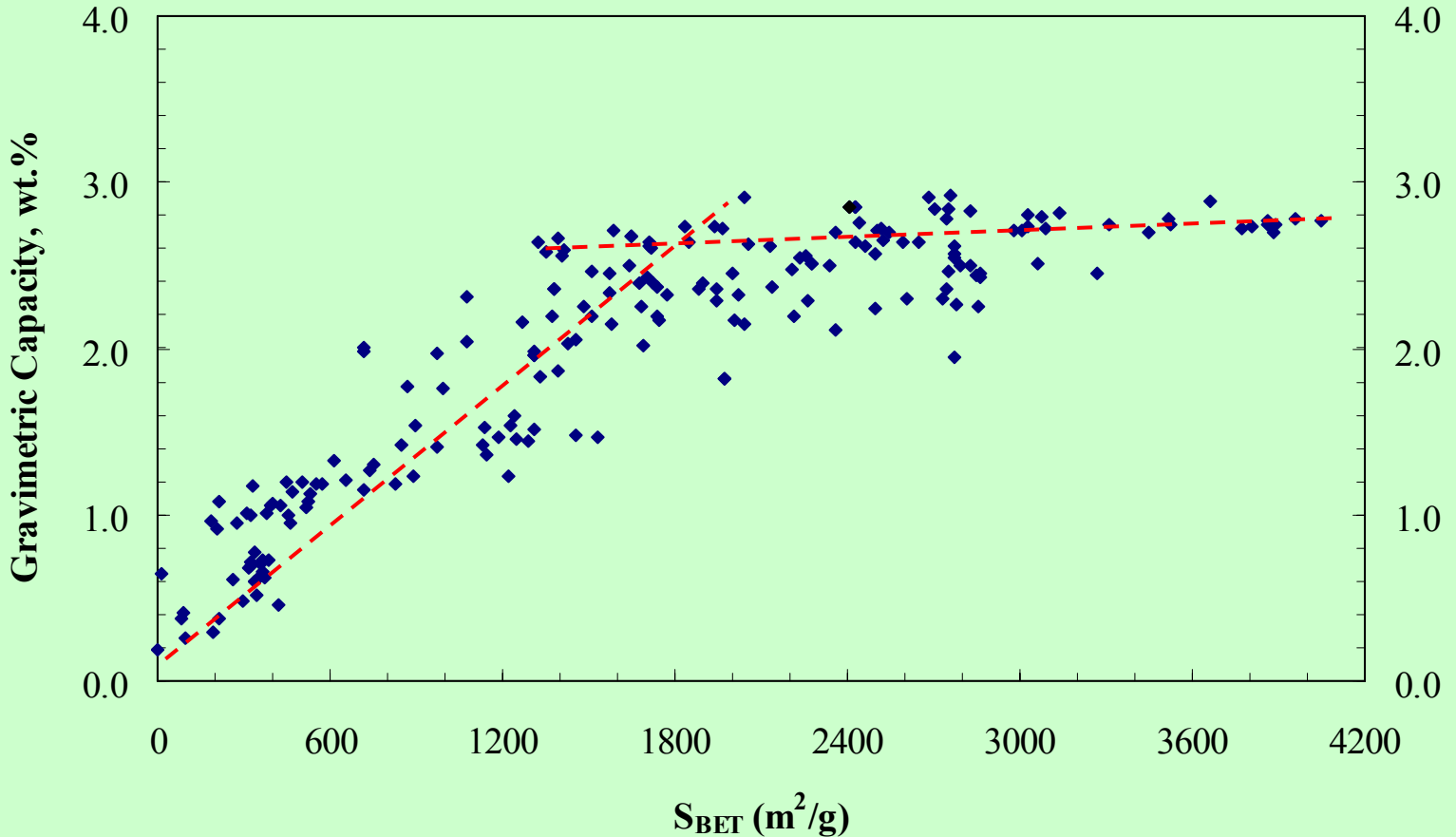


10-g batch synthesized carbons shows a variation of surface area $\pm 2.4\%$ and hydrogen capacity $\pm 2.0\%$ at 77 K and 1 bar.

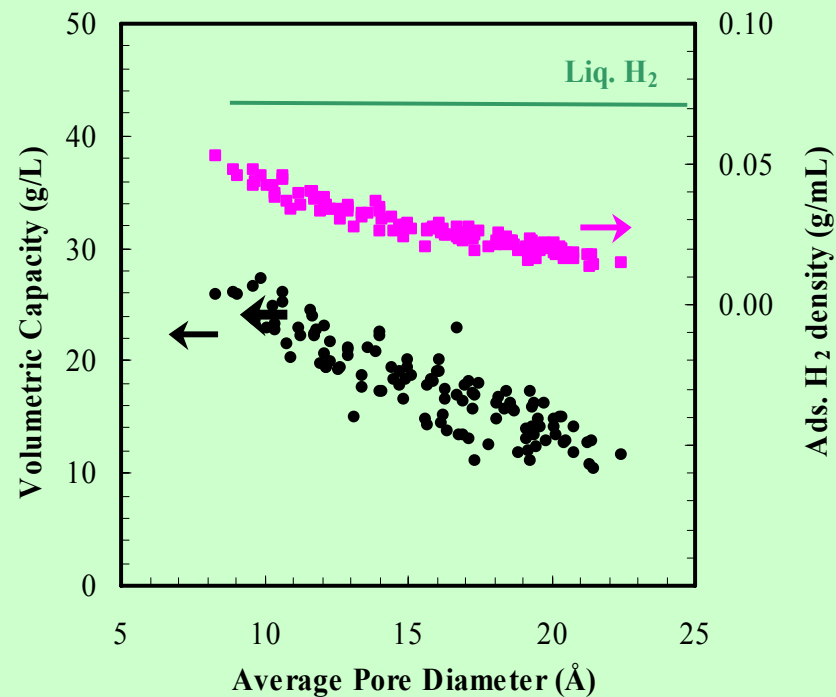
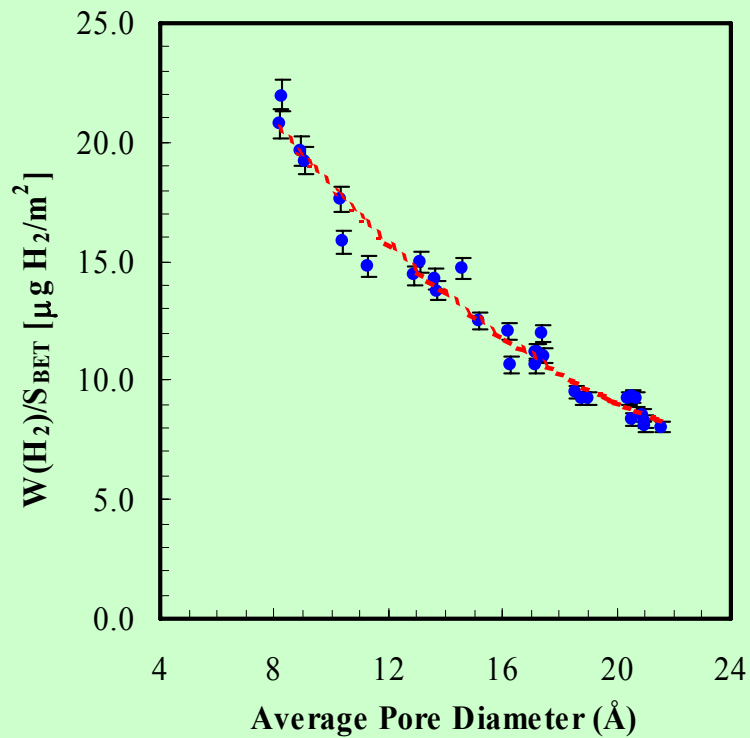


- Hydrogen sorption is reversible at 77 K and pressure up to 1 bar;
- Gravimetric and volumetric capacity both increase as average pore size decreases from 22 to 17 Å. (All carbon samples shown in the figures have a similar BET surface area of $\sim 2700 \text{ m}^2/\text{g}$);
- Small pore size is essential for high hydrogen storage capacity.

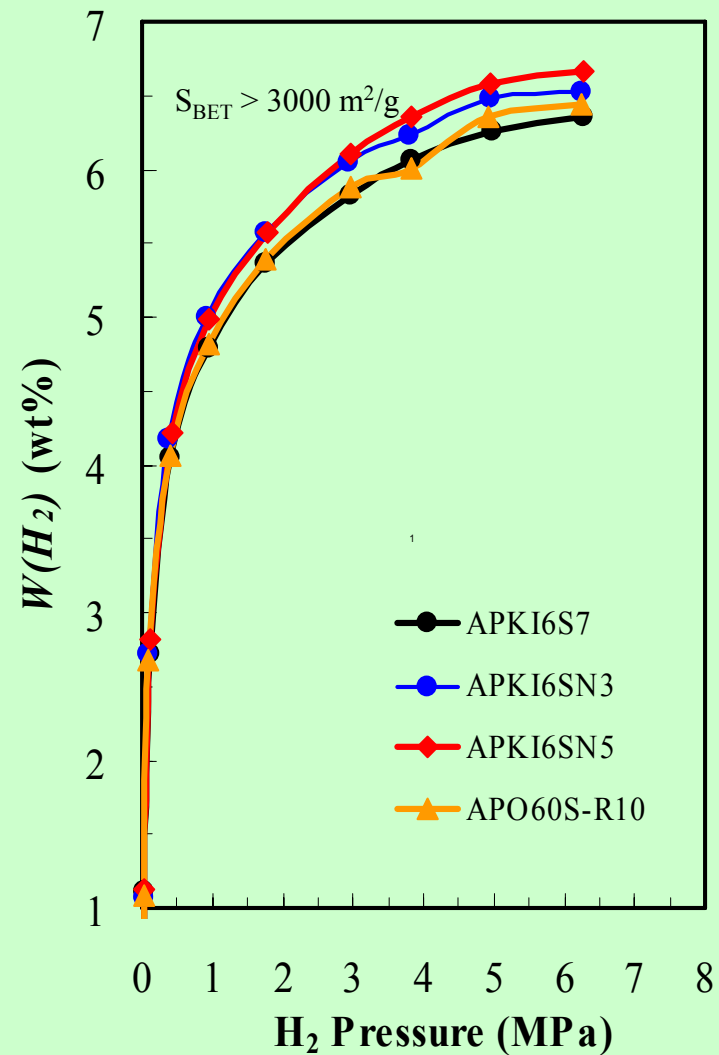
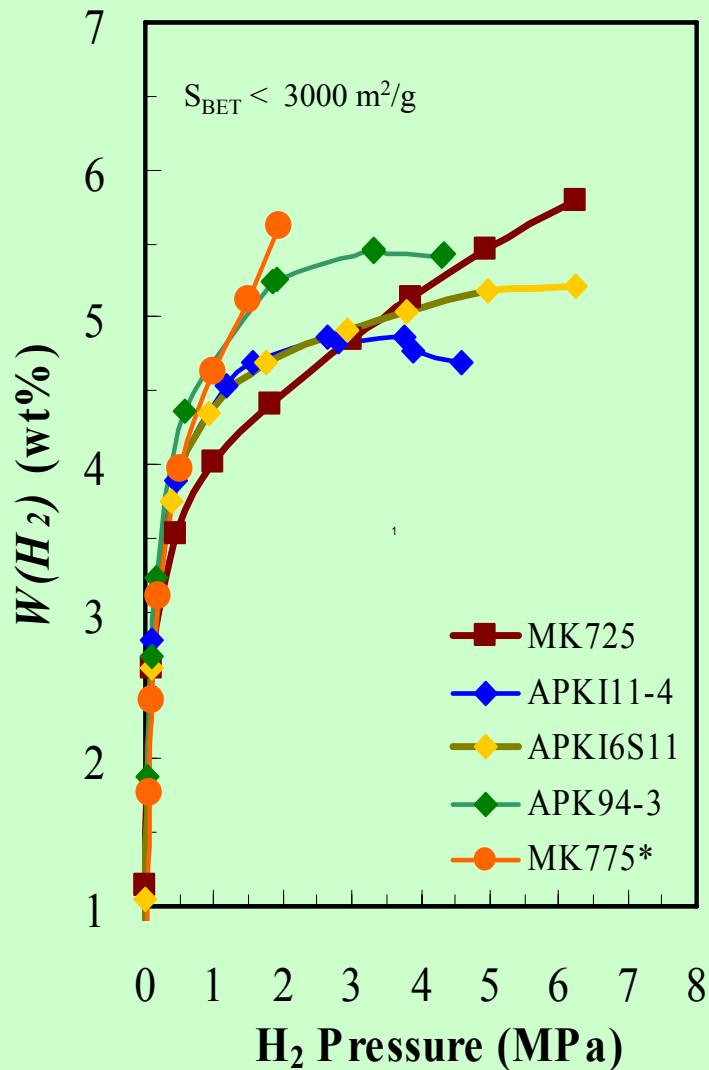
Correlation of Hydrogen Gravimetric Capacity With Specific Surface Area at 77 K and 1 Bar



- Gravimetric capacity increases as surface area increases at $\sim 19 \mu\text{g H}_2/(\text{m}_2/\text{g})$ below surface area of $\sim 1800 \text{ m}^2/\text{g}$;
- Gravimetric capacity of $\sim 3.0 \text{ wt}\%$ is achieved with surface area of $\geq 1800 \text{ m}^2/\text{g}$ 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.

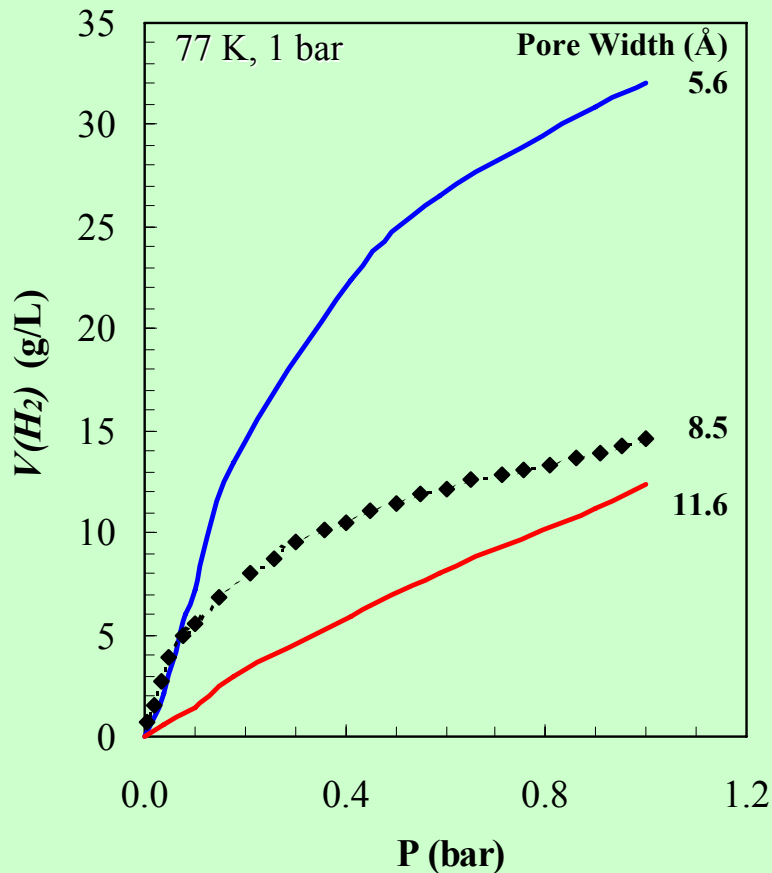


Excessive Hydrogen Uptake of Polymer Carbons at 77 K and High Pressure

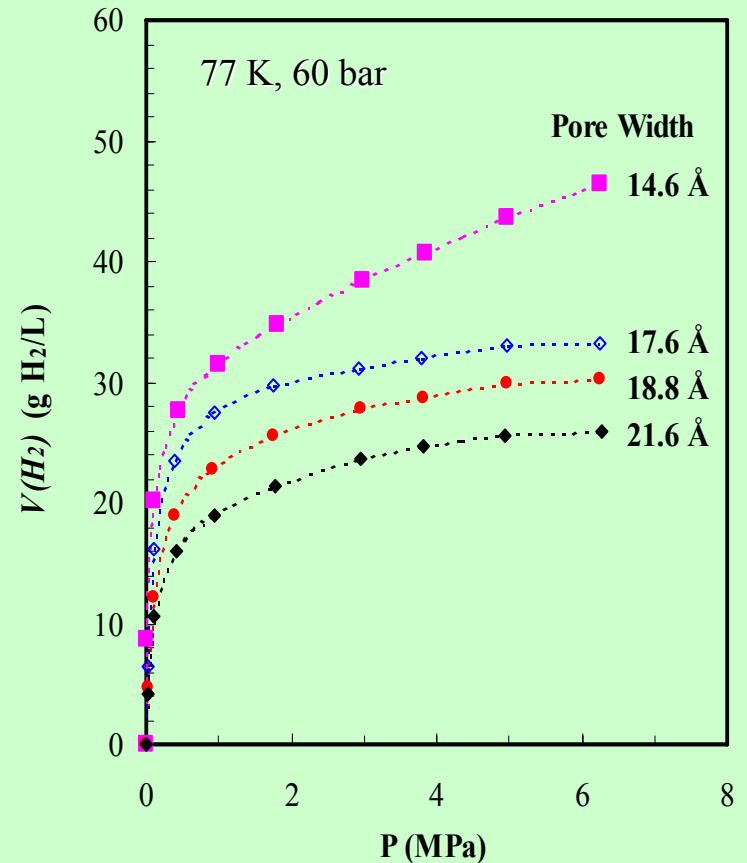
- The gravimetric storage capacity recorded up to $\sim 6.7 \text{ wt}\%$;
- Carbon samples synthesized in this laboratory were sent to multiple institutions for high pressure hydrogen uptake. The data show measurement conducted by: *Gas Technology Institute, Inc., Université du Québec à Trois-Rivières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

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

Impact of Pore Size on Hydrogen Volumetric Density

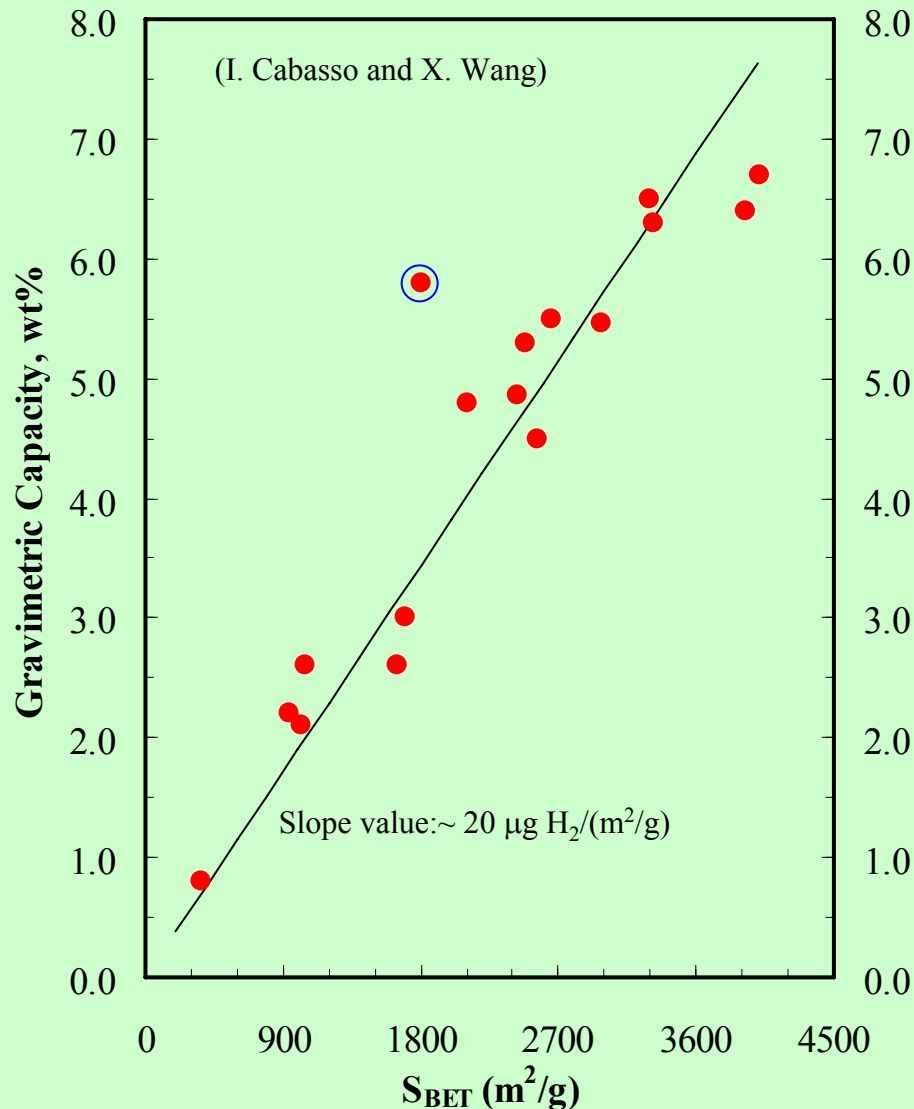


At 77 K and 1 bar, experimental hydrogen adsorption of polymer carbon with a pore width of ~ 8.5 Å falls between the computer simulated data for carbons having a pore width of 5.6 and 11.6 Å [Kowalczyk, et al., *Langmuir*, 2006, 22, 1970].



At 77 K and 60 bar, experimental data shows that decreasing the pore size increases H₂ 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 $\sim 20 \mu\text{g H}_2/(\text{m}^2/\text{g})$, which indicates $\sim 6 \text{ H}_2$ 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 ($S_{\text{BET}} \sim 4000 \text{ m}^2/\text{g}$, pore vol $\sim 2.30 \text{ mL/g}$).
- The circled sample has a microporosity of $\sim 96\%$ with an average pore width of $\sim 14.2 \text{ \AA}$, and exhibits a volumetric capacity of up to $45 \text{ g H}_2/\text{L}$.

Progress Project Summary

Hydrogen Storage Capacity of Polymer-Derived Carbon Nanostructures

Sample	Polymer	Porous Texture				H ₂ Storage, 77 K	
		S_{BET}^a (m ² /g)	Pore Vol. (mL/g) ^b	Microporosity (%)	d_{DR}^c (Å)	Gravimetric (wt%)	Volumetric ^d (g/L)
MK725*	PEEK	1800	0.87 (0.84)	96.6	14.6	5.8	(45)
APKI11-4	PEEK/PEI	2110	1.03 (0.98)	95.1	16.1	4.8	(33)
APKI6S11	PEEK/PEI	2480	1.20 (1.14)	95.0	17.6	5.3	(33)
APK94-3	PEEK	2650	1.54 (1.32)	85.7	20.2	5.5	(29)
MK775	PEEK	2680	1.15 (1.10)	95.1	17.2	5.6	(37)

Sample	Polymer	Porous Texture				H ₂ Storage, 77 K	
		S_{BET}^a (m ² /g)	Pore Vol. (mL/g) ^b	Microporosity (%)	d_{DR}^c (Å)	Gravimetric (wt%)	Volumetric ^d (g/L)
APKI6S7	PEEK/PEI	3320	1.67 (1.49)	89.2	19.1	6.3	(31)
APKI6SN3	PEEK/PEI	3300	1.85 (1.47)	79.5	18.8	6.5	(30)
APO60S-R10	PPO	3920	2.20 (1.72)	78.1	22.1	6.4	(25)
APKI6SN5	PEEK/PEI	4020	2.30 (1.75)	76.1	21.6	6.7	(26)

Summary

- **Demonstrated synthesis of 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 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 H₂ 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.